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FOREWORD

There is a growing awareness within the scientific community and amongst the public at large of environmental pollution resulting from human activities. Chemicals introduced into the atmosphere and transported on the winds can have deleterious effects on plants, animals and water supplies when they are deposited to the earth's surface. What previously was thought to be merely a local disturbance of the environment has often turned out to be of regional or even global significance. It is therefore important to monitor on a regional scale the occurrence of man-made substances in the atmosphere and in rain and snow deposited to the ground.

The difficulty of measuring the concentration of a substance reliably in precipitation depends on several factors including: (i) its reactivity with common sample collection and analysis container materials, (ii) its chemical and biological stability in solution, (iii) its concentration and (iv) its likelihood of contamination during sample collection, handling and analysis. For the limited number of substances related to the acid rain problem, a decade of research has led to the development of measurement methodologies that avoid the pitfalls just outlined. However, for the myriad of substances that are potentially toxic to the environment, such as certain heavy metals and organic compounds, reliable measurement methodologies have only begun to emerge.

The Air Quality Research Branch of Environment Canada operates the Canadian Air and Precipitation Monitoring Network (CAPMON) to measure the total deposition of atmospheric trace substances in environmentally sensitive areas. To date, the focus has been on acid-related substances but there is now a growing concern for the deposition of toxic chemicals including heavy metals. Furthermore, there is a possibility that the trace metals content of precipitation can yield information on the source of pollution.

An international workshop on measurement of metals in precipitation was held in January 1986 at the Atmospheric Environment Service. The objective was to review current techniques of precipitation collection and analysis for environmentally important trace elements other than major ions, as well as to decide on which elements are currently suited to routine network measurements at rural and remote locations and which ones require more methodology development. The workshop took the form of a one-day mini-conference featuring invited speakers and a second day of working group deliberations. The workshop proceedings consist of the papers presented, followed by a summary of the integrated conclusions of the working groups. I would like to thank all participants, Dr. W. Schroeder, Ms. P. Pearson, Ms. M. Stasyshyn and Mr. B. Martin for making the workshop a success.

THE BIOLOGICAL IMPORTANCE OF METALS IN THE AQUATIC ENVIRONMENT

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INTRODUCTION

One of the major concerns related to the mobilisation transport and deposition of metals in the environment is for the well-being of biota in aquatic ecosystems. A related concern is for human health, which can be affected by metals directly from air, water or food, but which can also be affected by metals which have been "processed" by ecosystems. Some of the most dramatic metal poisoning incidents, such as Minimata disease (methyl mercury poisoning) and Itai-Itai disease (cadmium poisoning) were manifestations of metal toxicity enhanced by biotic processes in the ecosystem. In this brief review, some important factors influencing the effects of metals on biological activity will be considered, with special reference to the context of the importance of metals in precipitation.

By way of introduction, it should be noted that a number of metals are essential as nutrients for all living organisms. Their functions are reasonably well understood, at least for some metals, and they play key roles, e.g. as enzyme cofactors (e.g. copper and zinc) in redox reactions (e.g. iron and manganese) as constituents of biologically significant pigments (e.g. magnesium in chlorophyll, iron in hemoglobin) and as components of vitamins (e.g. cobalt in vitamin B₁₂). Such metals stimulate biological activity. Other metals, notably lead, cadmium and mercury, have absolutely no known biological function, and these are consistently toxic. Even those metals which behave as nutrients, sometimes referred to as

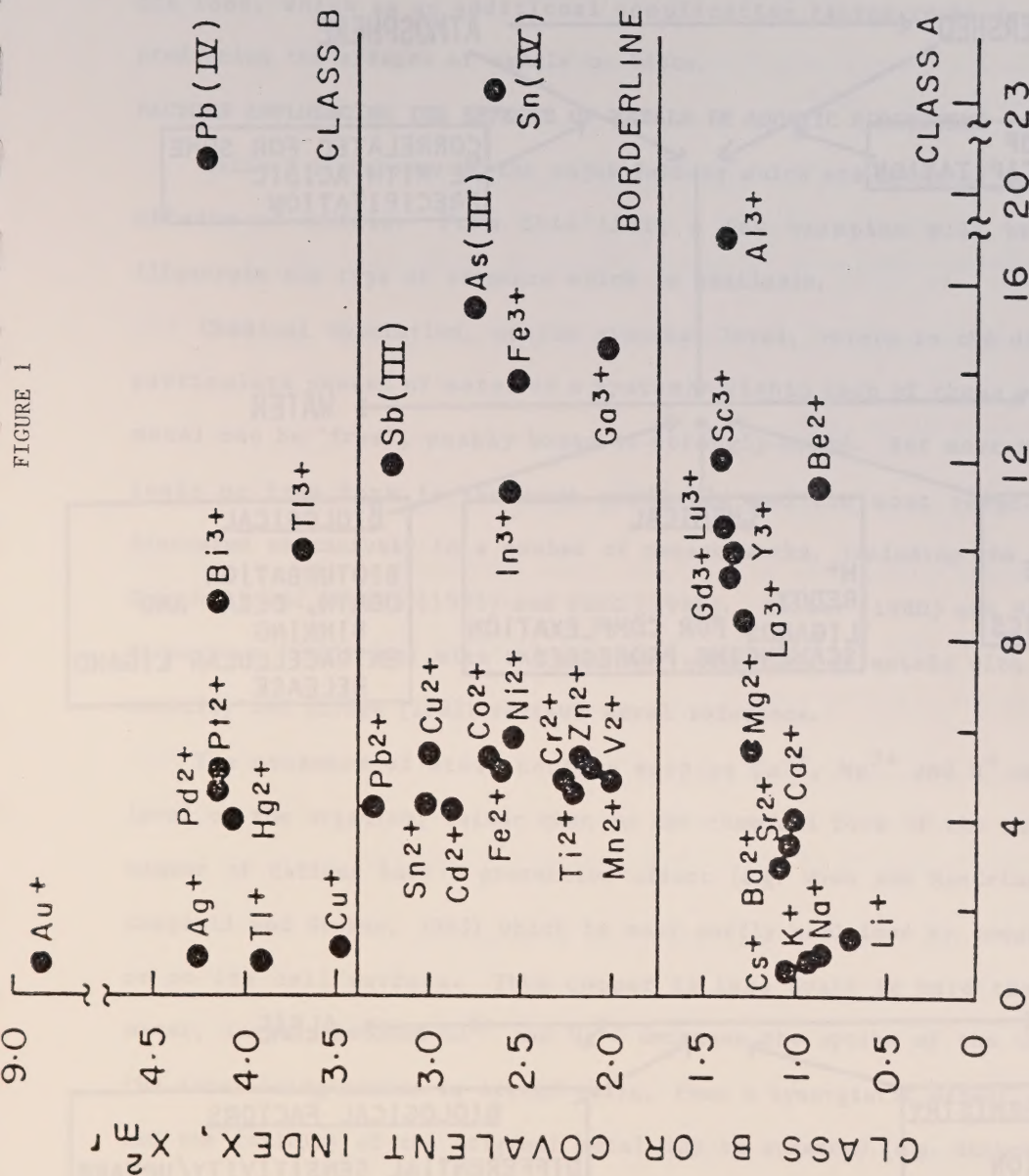
essential elements, can be toxic at higher concentrations (e.g. copper and zinc).

To a certain extent, the behaviour of a metal in a biological system can be predicted from its chemical and physical properties. Thus Nieboer and Richardson (1980) using a modification of the Irving-Williams series, classify metals as class A, (alkali and alkaline earths, e.g. Ca^{2+} , Na^{2+}) class B (transition metals, e.g. Hg^{2+} , Ag^{2+}) or "borderline" (Fe^{2+} , Mn^{2+} , Cu^{2+}). Figure 1 summarises the basis of their classification. Class B metals seek sulphur rather than oxygen, and thus tend to block essential SH groups on proteins. These are the highly toxic elements. Class A on the other hand are oxygen or nitrogen seeking, are benign in contrast to class B, and include the essential nutrient cations. Borderline metals include those which are required in trace quantities but which are toxic at higher concentrations. In a similar approach, Kaiser (1980) was able to predict or at least rank the toxicity of metals to aquatic biota by using a relatively small number of physico chemical properties of the elements.

Even at this level of prediction, which is based upon relatively simple systems of inorganic milieux, there are uncertainties. For example, these "bio-inorganic" considerations do not include kinetic effects, which may be profoundly important in biological systems, with their internal compartmentalization of complex membrane-bound organelles as well as membrane-bounded interfaces with the environment. And superimposed upon this level of uncertainty are the complexities of the biological and chemical processes occurring outside the organism, in the ecosystem. Predictions about the behaviour and biological effect(s) of a metal have to take into account a number of intrinsic and extrinsic factors.

Figure 2 illustrates the factors influencing the transfer of metal from

FIGURE 1



CLASS A OR IONIC INDEX, Z^2/r

A separation of metal ions and metalloids into three categories: Class A, borderline and Class B. The Class B index X^2/r is plotted for each ion against the Class A index Z^2/r . In these expressions, X_m is the metal-ion electronegativity, r its ionic radius and Z its formal charge. Oxidation states given by Roman numerals imply that simple cations do not exist even in acidic aqueous solutions (Nieboer and Richardson, 1980).

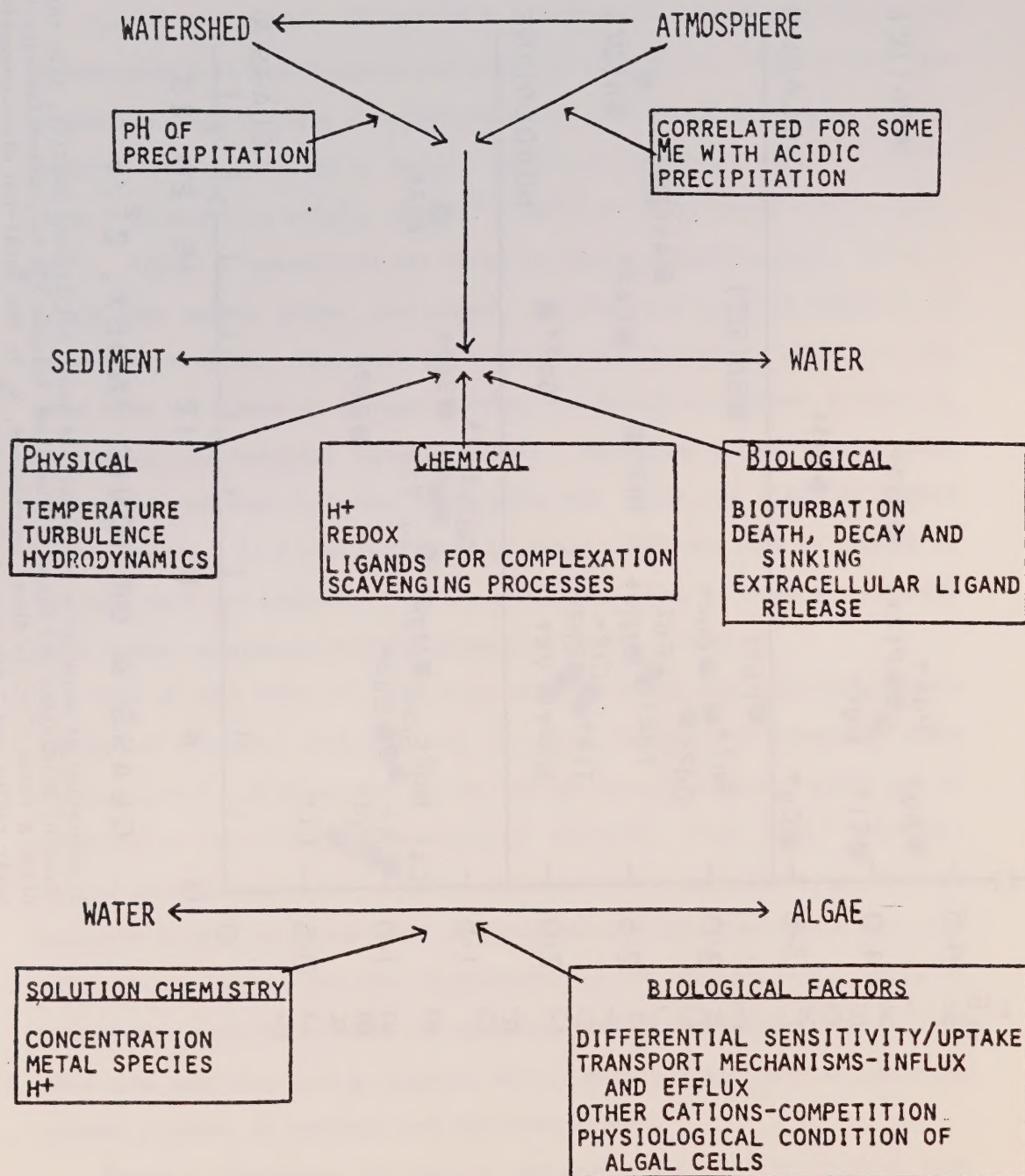
PATHWAYS OF METALS TO ALGAE

FACTORS INFLUENCING TRANSFER

LOADING-EXTERNAL TO BASIN

ALGAL ENVIRONMENT

ALGAL UPTAKE



the atmosphere to a simple primary producer in an aquatic system (Stokes et al., 1985). For a consumer, there is an additional vector or pathway, namely the food, which is an additional complicating factor to be considered in predicting the effects of metals on biota.

FACTORS INFLUENCING THE EFFECTS OF METALS IN AQUATIC ECOSYSTEMS

Table 1 lists some of the major factors which are known to influence the effects of metals. From this list, a few examples will be drawn to illustrate the type of evidence which is available.

Chemical speciation, at its simplest level, refers to the dissolved vs particulate phases of metal in a system. Within each of these phases, the metal can be "free", weakly bound or strongly bound. For most metals, the ionic or free form is the most available and the most toxic. This is discussed extensively in a number of recent works, including the reviews of Campbell and Stokes (1985) and NRCC (1986). Kaiser (1980) and Nieboer and Richardson (1980) deal with the inherent properties of metals with respect to toxicity and Stokes (1983) reviews metal tolerance.

The presence of other cations such as Ca^{2+} , Mg^{2+} and H^+ acts at the level of the organism, rather than on the chemical form of the metal, and a number of cations have a protective effect (e.g. Wren and MacCrimmon, 1983; Campbell and Stokes, 1985) which is most easily explained by competition at or on the cell surface. Thus copper is less toxic in hard than in soft water, largely because Ca^{2+} and Mg^{2+} decrease the uptake of the copper. If the interacting cation is itself toxic, then a synergistic effect may result and the toxicity of the original metal may be enhanced (e.g. Stokes, 1975).

The organic content of the water is an important factor in that metal-organic complexes are usually much less toxic than the free ionic form of the metal (e.g. Chau et al., 1975); however for mercury the reverse is true in

TABLE 1

SOME FACTORS INFLUENCING EFFECTS
OF METALS IN ECOSYSTEMS

- . Source (air, water)
- . Duration and rate of input (pulse, continuous)
- . Chemical speciation in source (dissolved, complexed, solid)
- . Inherent properties of metal (electronegativity, ion radius)
- . Concentration (dose, toxicity)
- . Past history of contamination (selection for tolerance, accumulation)
- . Geochemistry of soils and sediments (particle size, organic content, calcium content)
- . Other cations in water (Ca, Mg, H)
- . Organic content of water (complexation, alkylation)
- . Biological activity (bioturbation, productivity)
- . Morphometry (lake depth, shoreline development, watershed area)
- . Management practices (dredging, flooding, cultivating)

that the methylated form is much more available, more toxic and has a longer residence time in the body, than the inorganic form (Kaiser and Tolg, 1980). Methylation of mercury is normally promoted by organic matter. Therefore, one cannot make a blanket statement that increased organic content decreases metal toxicity.

Much of the metal in the aquatic system resides in the sediments. While sediments are frequently sinks for metals, physical disturbance and sometimes chemical changes resulting from biological or other activities in the sediment, or at the sediment-water interface, can promote the release of metals into the overlying water. One such process is bioturbation, the physical and chemical manifestation of the activities of the burrowing (infaunal) community (Krantzberg, 1985).

THE RELATIONSHIP BETWEEN LONG RANGE TRANSPORT OF ATMOSPHERIC POLLUTANTS AND THE BIOGEOCHEMICAL CYCLING OF METALS

In a recent survey of the influence of acidification and long range transport of atmospheric pollutants on the cycling of metals, Campbell et al (1983) reviewed three major sources of variation. The first was the influence of man's activities on the atmospheric movement of metals, the second involved the chemical changes in terms of mobility and speciation of the metal resulting from acidification and the third was the biological significance of the metal in terms of its tendency to be toxic or to bioaccumulate in living tissue. Table 2 summarises their findings. In response to the question, "which metals should we be concerned about?" (especially in the context of acidification), they concluded that Al, Cd, Cu, Hg, Mn, Pb and Zn were definitely of concern. For other metals, including As, Be, Mo, Sn and Te, although these had been identified as toxic and of environmental significance (Wood, 1975), the authors considered that they

Table 2 Metals of concern in relation to acidification of surface waters.^a

Metal ^b	Atmosphere anthropogenic control ^c	Over the range pH 4-7		Toxicity ^f		Bioaccumulation observed ^g	
		Increased total concentration observed ^d	Speciation change ^e		Observed in acid lakes		
			Calculated	Observed	Inherent		Observed in acid lakes
Ag [†]	+				+		
Al [*]		++	+	+	—		
As	+						
Be [*]							
Cd [†]	+	+		+	+	+	
Co [*]	+						
Cu [*]	+		+	+	+		
Hg [*]	+	+	+	+	—		
Mn	+	++	+				
Mo							
Ni [†]	+						
Pb [*]	+	+	+	+		+	
Se [†]	+						
Sn							
Te							
Tl [†]							
V [†]							
V [†]	+	++		+	+		
Zn [*]	+	++	+				

^a Data of Campbell et al. (1).^b Symbols: * denotes sufficient evidence to warrant concern; † denotes insufficient evidence; no symbol denotes evidence suggests no problem in the context of acidification.^c Are metal concentrations in the atmosphere controlled by human activities?^d Do metal concentrations increase in response to acidification, in either the soil or the aquatic environment, i.e., does mobility increase?^e Does a pH change from 7 to 4 cause significant changes in metal speciation?^f What is the inherent toxicity of the metal? (13): ++ = highly toxic; + = moderately toxic; — = very low toxicity.^g Does the metal have a tendency to bioaccumulate in response to acidification?

Source: Stokes et al., 1985.

were not likely to be problems in the context of acidification. Of course, this by no means excludes their potential for damage to biota, especially in point source situations. For the third set, which included Ag, Co, Ni, Se, Tl and V, the authors concluded that there was insufficient information to determine the potential for concern and more research was required.

CONCLUSION

While our information base is very incomplete in terms of the chemistry and more particularly the biochemistry of the potentially toxic metals, evidence is accumulating to suggest that a "warning signal" should be given for a number of these metals. Cases of chronic poisoning to man, or even to other biota, are admittedly rare except or relatively massive releases of metals at point sources, through accidents or industrial exposure. But with foresight, it is prudent to limit, wherever possible, the further release or mobilisation of metals into the environment.

REFERENCES

- Bailey, R.C. and P.M. Stokes. 1984. Evaluation of filamentous algae as biomonitors of metal accumulation in softwater lakes: Multivariate approach. Aquatic Toxicology and Hazard Assessment: Seventh Symposium. ASTM STP 854, R.D. Cardwell, R. Purdy and R.C. Bahner (eds.) American Society for Testing and Materials, 1984. pp. 5-26.
- Campbell, P.G.C. and P.M. Stokes. 1985. Acidification and toxicity of metals to aquatic biota. Can. J. Fish. Aquat. Sci. 42: 2034-2049.
- Campbell, P.G.C., P.M. Stokes and J.N. Galloway. 1983. Effects of atmospheric deposition on the geochemical cycling and biological availability of metals. 4th Inter. Conf. on Heavy Metals in the Environment, Heidelberg, Germany, CEP Consultants, Sept. 6-9, 1983. pp. 760-763.
- Chau, Y.K., R. Gachter and K. Lum-Shue Chan. 1974. Determination of the apparent complexing capacity of lake waters. J. Fish. Res. Bd. Can. 31: 1515-1519.
- Kaiser, K.L.E. 1980. Correlation and prediction of metal toxicity to aquatic biota. Can. J. Fish. Aquat. Sci. 37: 211-218.
- Kaiser, G. and G. Tolg. 1980. Mercury. In Hutzinger, O. (ed.) The Handbook of Environmental Chemistry, Vol. 3, Part A, Anthropogenic Compounds, pp. 1-43. Springer-Verlag Publishers.
- Krantzberg, G. 1985. The influence of bioturbation on physical, chemical and biological parameters with emphasis on freshwater environments: a review. Environ. Pollut. (A) 39: 99-122.
- Nieboer, E. and D.H.S. Richardson. 1980. The replacement of the nondescript term "heavy metals" by a biologically and chemically significant classification of metal ions. Environ. Pollut. (B): 1: 3-36.
- Campbell, P.G.C. and A. Lewis (co-eds.) 1986. Biologically available metals in sediments. NRC Report #XXX. Associate Committee on Scientific Criteria for Environmental Quality (under review).
- Stokes, P.M. 1975. Uptake and accumulation of copper and nickel by metal-tolerant strains of Scenedesmus. Verh. Internat. Verein. Limnol. 19: 2128-2137.
- Stokes, P.M. 1983. Response of freshwater algae to metals. In Round, F.E. and D.J. Chapman (eds.) Progress in Phycological Research, Vol. 2, Chapter 3, pp. 87-112. Elsevier Science Publishers.
- Stokes, P.M., R.C. Bailey and G.R. Groulx. 1985. Effects of acidification on metal availability to aquatic biota, with special reference to filamentous algae. Env. Health Persp. 63: 79-87.

Wren, C.D. and H.R. MacCrimmon. 1983. Mercury levels in the sunfish Lepomis gibbosus, relative to pH and other environmental variables of Precambrian Shield Lakes. Can. J. Fish. Aquat. Sci. 40: 1737-1744.

Wood, J.M. 1974. Biological cycles for toxic elements in the environment. Science (Wash., D.C.) 183: 1049-1052.

COLLECTION AND ANALYSIS OF TRACE METALS IN CONTINENTAL PRECIPITATION
AT FORESTED SITES IN THE SOUTHEASTERN UNITED STATES^{1,2}

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ABSTRACT

Noncontaminating methods for collection and analysis of Cd, Mn, Pb, and Zn in rain were developed and applied to a study of metal deposition at four forested sites during the period 1976-1982. The metal concentrations measured in rain indicate that these sites are representative of rural, continental areas. The concentrations display both temporal and spatial trends, although the trends are complicated by the strong influence of rainfall amount which is inversely correlated with metal concentrations.

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INTRODUCTION AND METHODS

The fate of airborne pollutants is controlled by wet and dry removal mechanisms. Wet deposition is particularly important because of its episodic nature and because its components are delivered to the receptor partly in solution, thereby enhancing the possibility of biological interaction. For predictive purposes, there is a need to understand the behavior of constituents in rain. This paper describes sampling methodology and measurements of Cd, Mn, Pb, and Zn concentrations in rain collected in the southeastern United States. Sampling sites are located in rural areas of the southern Appalachians, characterized by mature mixed oak and hickory forests: Walker Branch experimental watershed (WB) in Oak Ridge, Tennessee (lat. 35°58'N, long. 84°17'W); Camp Branch (CB) and Cross Creek (CC) watersheds, ~100 km and 160 km to the southwest of WB respectively; and Coweeta Hydrologic Laboratory (CO), North Carolina, ~130 km to the southeast of WB.

We previously published details of our techniques for collection and analysis of wetfall-only on an event basis (Lindberg et al. 1977; Hoffman et al. 1980; Lindberg 1982). We modified an automatic precipitation-activated sampler of the wet/dry design by using chemically inert construction materials and by rearranging component parts to minimize trace-level contamination of samples. Samples were collected directly in individual polyethylene bottles with funnels. Bottles for trace metal samples were soaked in 2 N HNO₃ and profusely rinsed with distilled-deionized water; those for sulfate and pH were soaked and rinsed with distilled-deionized water only.

Samples were collected either above the forest canopy on 35 to 43-m meteorological towers (CC and CB in 1981-1982; WB in 1976-1977) or at ground-level clearings (CO and WB in 1981-1982). Bottles were sealed in the sampler against dry deposition for brief periods preceding rain and were collected within 24 h of the end of rain, minimizing exposure time in the field.

Trace metals were stabilized in unfiltered samples by acidification to pH ~ 1.2 with Ultrex ultra-pure HNO_3 . Because of the high water solubility of metals in atmospheric particles at these sites (Lindberg and Harriss 1983), additional dissolution of metals from particles after acidification is minimal. Concentrations were determined by graphite furnace atomic absorption spectrophotometry using the method of standard additions. Analytical precision and accuracy were checked in an interlaboratory comparison using precipitation "control standards," while combined sampling and analytical reproducibility were determined from replicate sampling of four separate precipitation events at one site with the following results: Pb, $\pm 5\%$; Mn, $\pm 10\%$; Cd and Zn, $\pm 15\%$ (average coefficient of variation, details in Lindberg et al. 1977).

During 1976 and 1977 we collected 68 event samples representing 76% of the total precipitation input. We defined an event as precipitation bracketed by 6-h periods of no measurable (< 0.25 mm) precipitation. By this definition the data set includes 32 samples of well-defined single storm events and 36 samples of generally closely spaced multiple events (2-6 events each, average of ~ 3). Less than 2% of the sampled precipitation occurred as snow. Rainfall amount, intensity, and duration

were measured using a combination of plastic wedge gauges and recording, weighing, and tipping bucket gauges. During 1981-1982, weekly or biweekly wet-only samples were collected and handled similarly (Lindberg and Turner 1983).

RESULTS AND DISCUSSION

In general, rain in inland regions of the southeastern United States, such as that measured at these sites, is a dilute mineral acid solution, primarily H_2SO_4 at pH 4.1 to 4.5. Concentrations of Cd, Mn, Pb, and Zn in rain at the four sites (Table 1) are comparable to those measured in other rural areas in North America (see other data in this workshop report). These metals comprise <1% of the total cation equivalents in rain, whereas H^+ contributes 50 to 60% of the cation equivalents and SO_4^{2-} contributes 60 to 70% of the anion equivalents (Lindberg 1982).

The mean concentrations of the metals are similar among the four sites for the 1981-1982 period. However, a Duncan-Waller K-ratio test revealed that the arithmetic means for Cd and Pb are significantly different ($P < 0.05$) among sites. For both elements, the major differences are between the CB and CO sites (Table 1). Except for Zn at CB and CC, the four sites generally show higher arithmetic than rainfall-amount-weighted means. This pattern occurs because larger rainfall events generally exhibit lower metal concentrations than do smaller rainfall events (see below).

Overall, the multisite comparison indicates that the WB site, with the longest observation period, is typical of rural sites in the region

Table 1. Trace metals concentrations in rain at rural, forested sites in the southeastern United States

Metal	Parameter	Concentrations (in $\mu\text{g/L}$)				
		Site ^a				
		WB-1	WB-2	CB	CC	CO
Cd	$\bar{x}$	0.42	0.14	0.41	0.28	0.07
	σ	0.49	0.17	0.83	0.30	0.09
	Range	0.003-2.2	0.01-0.97	0.02-4.1	0.04-1.3	0.01-0.63
	Weighted $\bar{x}$	0.25	0.08	0.24	0.21	0.041
Mn	$\bar{x}$	3.6	3.7	4.4	4.1	2-8
	σ	5.2	4.4	4.9	4.1	4.2
	Range	0.03-24	0.2-26	0.3-21	0.3-19	0.2-26
	Weighted $\bar{x}$	1.9	2.3	3.2	2.7	1.3
Pb	$\bar{x}$	6.8	5.0	7.0	6.2	4.5
	σ	5.3	4.3	5.4	5.1	4.1
	Range	0.66-24	0.5-31	0.5-26	1-26	0.6-23
	Weighted $\bar{x}$	5.2	4.0	5.6	4.8	3.2
Zn	$\bar{x}$	5.6	6.9	7.6	5.9	10.3
	σ	5.8	9.7	13	8.1	18
	Range	0.44-30	0.2-67	0.3-63	0.5-41	0.4-90
	Weighted $\bar{x}$	5.0	4.9	10.2	8.7	8.6

^aWB-1 = Walker Branch, Tennessee, 1976-1977 (n = 52); WB-2 = Walker Branch, Tennessee, 1981-1982 (n = 70); CB = Camp Branch, Tennessee, 1981-1982 (n = 36); CC = Cross Creek, Tennessee, 1981-1982 (n = 36); CO = Coweeta, North Carolina 1981-1982 (n = 70).

with respect to metal concentrations in rain. The proximity (within 20 km) of the WB site to two large and three small coal-fired power plants has not been manifested in significantly higher rain concentrations of metals (Lindberg 1982).

We can compare metals in rain collected at the WB site during two periods: March 1975–November 1977 (event samples) and December 1980–July 1982 (weekly samples). Only 30% of the data from the latter period represented single-event samples. However, this difference in methodology should not preclude comparison of the seasonal trends for the two periods. Total rainfall during winter (Fig. 1) and summer was similar for the two periods, but rainfall during spring and autumn was slightly higher for the earlier period. As discussed below, metal concentrations vary more in response to the amount of rainfall per event than to the total monthly rainfall. Thus, these differences in monthly rainfall between the periods are not expected to affect metal concentrations ($\mu\text{g/L}$), although they do affect metal deposition (mg/m^2).

For the earlier period, the concentrations of Mn, Pb, and Zn in rain exhibit similar seasonal trends, with highest concentrations occurring during warm weather periods (Mn and Pb summer, Zn fall, Fig. 1); Cd exhibited little seasonal variation. These trends were statistically significant ($P < 0.01$, ANOVA) for Mn (summer arithmetic mean concentration exceeded winter mean by a factor of 2.2), Zn (fall arithmetic mean exceeded winter by factor of 5.2), and Pb (summer/winter = 2.2), but not for Cd (summer/winter = 0.7). Similar trends have been reported for major ion concentrations in rain at WB and

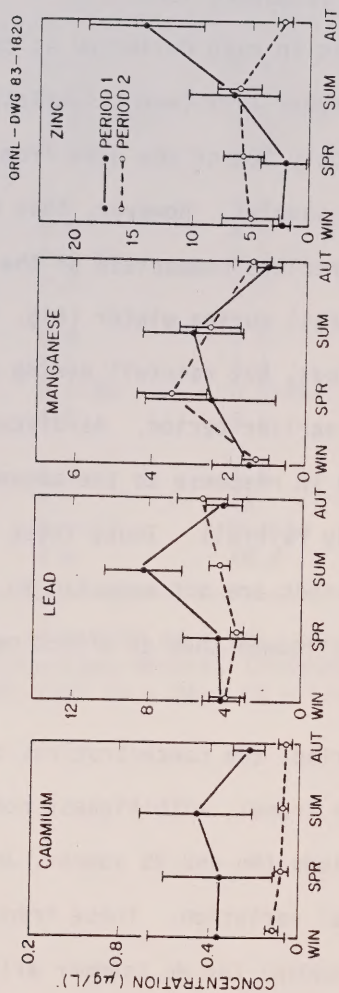


Fig. 1.

Rainfall-amount-weighted mean ($\pm$ S.E.) metal concentrations as a function of season and observation period. Seasons are: WIN =

December-February, SPR = March-May, SUM =

June-August, AUT = September-November.

Periods are: 1 = March 1975 - November 1977, and 2 = December 1980 - July 1982.

elsewhere, suggesting synoptic conditions as controlling factors (Lindberg 1982; Hendry and Brezonik 1980). A possible explanation is that the summer maxima are related to meteorologic conditions that result in elevated pollutant concentrations due to air stagnation, and in generally lower rainfall amounts per event and hence less dilution of rain-scavenged material. Except for Mn, seasonal patterns are less obvious during the more recent observation period. The collection of weekly and biweekly, rather than event samples, apparently obscures these patterns to some extent.

Based on Student's t-test analyses, the mean (arithmetic) concentration of Cd is significantly ($P < 0.05$) lower (by a factor of ~3) for the more recent period compared to that for the earlier period. Differences in the concentrations of the other metals between these periods are not significant ($P > 0.05$). Stratifying the data by season revealed that the earlier period exhibited (1) significantly higher mean Cd concentrations for all seasons, (2) significantly higher mean Pb concentrations only during the summer, and (3) significantly higher mean Zn concentrations only during the autumn. These findings suggest that regional emissions of Cd, and perhaps Pb and Zn, may have been reduced between 1975-1977 and 1980-1982. Over this period, emission control equipment was upgraded at two large nearby (20 km) coal-fired power plants, the use of leaded gasoline declined, and the fuel economy of vehicles increased. Others (Smith and Siccama 1981) showed recent declines in Pb concentrations in rain in the northeastern United States ($3.6 \mu\text{g/L}$ per year) which appear to correlate with reductions in vehicular emissions. For the WB site, annual weighted-mean Pb

concentrations have declined since 1975. These values are: 1975 (N = 9), 7.5 $\mu\text{g/L}$; 1976 (N = 23), 5.3 $\mu\text{g/L}$; 1977 (N = 32), 5.0 $\mu\text{g/L}$; 1981 (N = 47), 4.2 $\mu\text{g/L}$; and 1982 (N = 31), 3.8 $\mu\text{g/L}$ (Lindberg and Turner 1983).

An understanding of physical factors controlling rain chemistry is best gained by analysis of single event samples such as those collected at WB during 1976-1977. The following event characteristics may influence metal concentrations: rainfall amount (depth in cm), rain duration (wet period in h), rain intensity (cm/h), antecedent period (length of preceding dry period in h), and air mass trajectory. All of the metals except Zn exhibit significant ($P < 0.05$) negative correlation coefficients with rainfall amount (Lindberg 1982). The remaining correlation coefficients are also negative, although only those between duration and Cd and Mn concentrations are significant. Thus, as rainfall amount, duration, and intensity increase, there is a general decrease in rain concentrations, suggesting a dilution effect by increasing rainfall.

The relationship between rainfall amount and concentration appears to be the most uniform and significant of those investigated. The nonevent data collected at the four sites during 1980-1982 exhibited similar trends; all correlation coefficients between concentration and rainfall were negative and significant ($P < 0.05$) at the WB and CO sites, whereas all except those for Zn were negative and significant at the CB and CC sites. Others reported generally inverse correlations between intensity and major ion concentrations in rain; however, the most widely discussed effect is that of rainfall amount on concentration (e.g., Junge

1963). Several mechanisms could potentially explain these observations, including diffusive aerosol capture, initial rain evaporation, dilution of initially scavenged material by heavy rain, and depletion of below-cloud aerosols as rainfall continues.

RESEARCH NEEDS

Quantification of the wet component of atmospheric metal deposition is much more addressable with current methodologies than is the dry component, as indicated by recent workshops and symposia (Hicks et al. 1980; Pruppacher et al. 1983). In part as a result of the interest in precipitation chemistry generated by the acid rain phenomenon, there have been several studies concerned with development of precipitation sampling and analytical methodology for major and trace components (see the review by Lindberg and McLaughlin, in press).

It is my opinion that the most important research needs in the field of metal wet deposition concern the design of field experiments for collection of data appropriate for improving our understanding of deposited metal interactions with the biosphere. These research needs have been summarized elsewhere (Hosker and Lindberg 1983; Lindberg and McLaughlin, in press). There are also several aspects of the physical collection of wet deposition that need to be addressed in future studies:

1. Methods for contamination-free collection of precipitation for trace organic and inorganic analyses should be further refined to ensure that high quality samples can be collected on a routine basis.

2. Regional-scale multisite studies are needed to determine the representativeness of single-site measurements.
3. Input from meteorologists is needed on the ancillary observations or measurements that should be made during precipitation collection.
4. Methods should be developed for routine collection of intercepted fog.
5. Metal solubility studies in rain are needed to assess the relative importance of particulate components in precipitation. Hence, samplers should be designed to reliably filter precipitation as it is collected.
6. Input from plant physiologists is needed on the most appropriate time scale for collection of precipitation data (subevent, event, weekly.)
7. Further work is needed to assess the effects of gas exchange on rain chemistry before samples are returned to the laboratory.
8. The wetness sensor head currently in use on wet/dry samplers needs to be redeveloped to provide more reliable operation, to ensure collection of the entire precipitation event, and to minimize the exposure time of the sampler to dry deposition.
9. Studies on the chemical stability of both rain and throughfall samples are needed.
10. Coordinated collection of cloud water and precipitation at several levels between the cloud base and the ground is needed to increase our understanding of scavenging mechanisms and gas-particle interactions with precipitation.

REFERENCES

- Hendry, C. D., and P. L. Brezonik. 1980. Chemistry of precipitation in Gainesville, Florida. Environ. Sci. Technol. 14:843.
- Hicks, B. B., M. L. Wesely, and J. L. Durham. 1980. Critique of methods to measure dry deposition: Workshop summary. EPA 600/9-80-050. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.
- Hoffman, W. A., S. E. Lindberg, and R. R. Turner. 1980. Precipitation acidity: The role of the forest canopy in acid exchange. J. Environ. Qual. 9:95-100.
- Hosker, R. P., and S. E. Lindberg. 1982. Review article: Atmospheric deposition and plant assimilation of airborne gases and particles. Atmos. Environ. 16:889-910.
- Junge, C. E. 1963. Air Chemistry and Radioactivity. Academic Press, New York.
- Lindberg, S. E., and S. B. McLaughlin. Current problems and future research needs in the acquisition, interpretation, and application of data in terrestrial vegetation--air pollutant interaction studies. IN A. Legge and S. V. Krupa (eds.), Air Pollutants and Their Effects on the Terrestrial Ecosystem. John Wiley and Sons, New York (in press).
- Lindberg, S. E., and R. C. Harriss. 1983. Water- and acid-soluble metals in atmospheric particles. J. Geophys. Res. 88:5091-5100.

- Lindberg, S. E., and R. R. Turner. 1983. Trace metals in rain at forested sites in the eastern United States. pp. 107-144. IN Proceedings International Conference on Heavy Metals in the Environment. CEP Consultants Ltd, Publishers, Edinburgh, United Kingdom, 1284 pp.
- Lindberg, S. E. 1982. Factors influencing trace metal, sulfate, and hydrogen ion concentrations in rain. Atmos. Environ. 16:1701-1709.
- Lindberg, S. E., R. R. Turner, N. M. Ferguson, and D. Matt. 1977. Walker Branch Watershed element cycling studies: Collection and analysis of wetfall for trace elements and sulfate. pp. 125-150. IN D. L. Correll, (ed.), Watershed Research in Eastern North American. Smithsonian Institution Press, Washington, D.C., 469 pp.
- Pruppacher, H. R., R. G. Semonin, and W. G. N. Slinn (eds.). 1983. Precipitation Scavenging, Dry Deposition and Resuspension. Elsevier Science Publ., New York, Vol. 2, pp. 837-848.
- Smith, W. H., and T. G. Siccama. 1981. Hubbard Brook ecosystem study: Biogeochemical cycles of Pb in a northern hardwood forest. J. Environ. Qual. 10:323-333.

RAIN COLLECTION PROCEDURE FOR THE UNIVERSITY OF RHODE ISLAND
TRACE METAL STUDIES

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INTRODUCTION

The Sea/Air Exchange (SEAREX) Program, which is sponsored by the National Science Foundation of the United States, is concerned with the atmospheric chemistry of trace metals and other substances over the Pacific Ocean. The general strategy of SEAREX has been to sample the four major surface level wind fields over the Pacific Ocean from 60°S to 60°N. Three experiments have been conducted for SEAREX so far; they were at Enewetak in 1979, at American Samoa in 1981, and at New Zealand in 1983 (Figure 1). The fourth and final experiment for SEAREX will take place in May, June, and July of 1986, and during that experiment samples will be collected from a ship in the westerly wind field of the North Pacific.

For SEAREX, our research group has determined the concentrations of selected trace elements in aerosol particle samples and rain water samples from the remote marine atmosphere (Duce et al., 1983; Arimoto et al., 1985). We have investigated the sources for trace metals by comparing elemental ratios observed in the samples with the corresponding ratios in reference materials. Sodium and aluminum are considered representative of sea salt and mineral aerosol, respectively, and enrichment factors for the trace elements are calculated according to the following formulae:

$$EF_{\text{sea}} = (Z/\text{Na}) \text{ in the sample} / (Z/\text{Na}) \text{ in bulk sea water}$$

and

$$EF_{\text{crust}} = (Z/\text{Al}) \text{ in the sample} / (Z/\text{Al}) \text{ in average crustal rock,}$$

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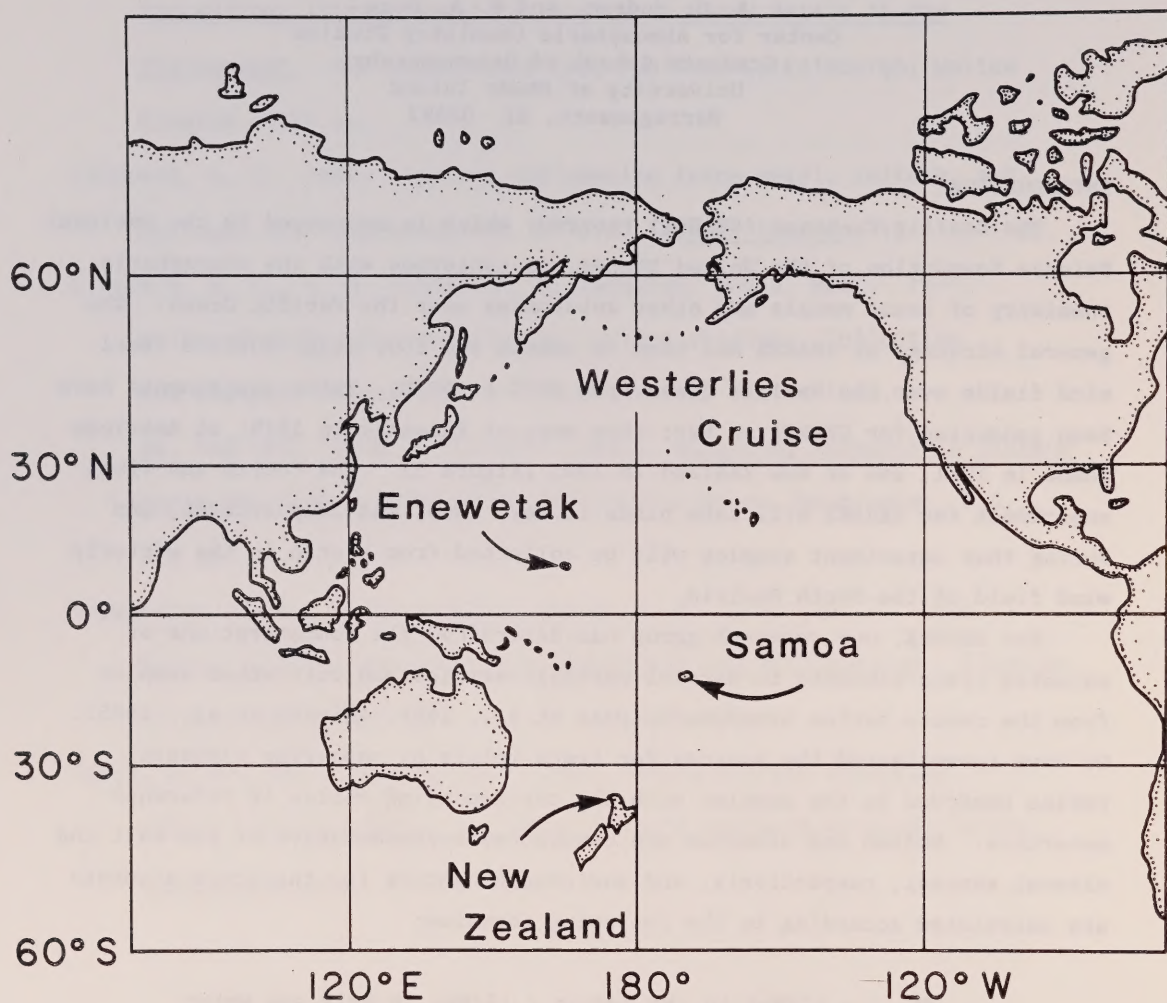


Figure 1. Station Locations for the Sea/Air Exchange (SEAREX) Experiments.

where EF_{sea} and EF_{crust} are the enrichment factors calculated relative to bulk sea water and average crustal rock, and Z denotes the element of interest. If the EF_{sea} or the EF_{crust} for an element approaches unity, then we infer that sea water or crustal rock, respectively, is the dominant source for the element.

Enrichment factors that were calculated from the data from Enewetak (Duce et al., 1983; Arimoto et al., 1985) have shown that Al, Sc, Mn, Fe, Co, Cs, Ba, Ce, Eu, Hf, Ta, and Th are predominantly from mineral aerosol, which is produced by the weathering of the continental crust. A second group of elements, Na, Mg, Ca, K, Cl, and Br is mainly derived from sea salt. A third group of elements, including Zn, Se, Ag, Cd, Sb, Cu, I, and Pb, is enriched relative to bulk sea water and crustal rock. The sources for the third group of elements are varied, but even at remote islands in the Pacific Ocean the impact of anthropogenic sources on the concentrations of some of these elements is apparent. For example, pollutant inputs of lead from smelters and automobile exhaust have caused the enrichments of this element even at Enewetak and Samoa (Settle and Patterson, 1982; Duce et al., 1983; Arimoto et al., 1985). The results obtained from these and other remote sites suggest that anthropogenic inputs of Zn, Sb, As, and Cd have also contaminated the global troposphere (Duce et al., 1976; Rahn, 1976; Meinert and Winchester, 1977; Buat-Menard and Chesselet, 1979; Maenhaut et al., 1981; Duce et al., 1983).

One of the major objectives of the SEAREX Program is to determine the atmospheric inputs of trace metals into the ocean, and therefore we are interested in the wet deposition fluxes of trace elements to the Pacific Ocean. The concentrations of trace elements at remote marine regions are far lower than in continental areas, of course (Table 1), and we must take extraordinary precautions to prevent the contamination of the samples. The following outline briefly describes the cleaning and collection procedures that the University of Rhode Island research team will use for the sampling of rain for trace elements during the SEAREX cruise in the North Pacific. The techniques described below are based on methods developed by Settle and Patterson (1982) of the California Institute of Technology. These procedures certainly would not be practical for routine monitoring, but certain aspects of the procedure could be adapted for such studies.

TABLE 1. Comparison of the Concentrations ($\mu\text{g kg}^{-1}$) of Trace Elements in Precipitation From Various Regions

Element	Enewetak*	Bermuda**	Urban†	Rural†
Aluminum	2.1			
Bromine	7.1			
Cadmium	0.0021	0.06	0.7	0.5
Calcium	50	310		
Chlorine	2,000	6,800		
Copper	0.013	0.66	41	5.4
Iodine	1.2			
Iron	1.0	4.8		
Lead	0.035	0.77	44	12
Magnesium	170	490		
Manganese	0.012	0.27	23	5.7
Potassium	39	160		
Scandium	0.00023			
Selenium	0.021			
Silver	0.0056		3.2	0.54
Sodium	1,100	3,400		
Thorium	0.00091			
Vanadium	0.018		42	9
Zinc	0.052	1.15	34	36

* Arimoto et al. (1985).

** Jickells et al. (1984).

† Median values for continental regions compiled by Galloway et al., 1982.

GENERAL SAMPLING CONSIDERATIONS

Both unfiltered and filtered rain water samples will be collected on the SEAREX cruise in the North Pacific Ocean. Filtered samples will be collected to study the partitioning of trace elements between the dissolved and particulate phases. The rain sampling funnel (Figure 2) is made entirely of plastic, except for a boom attachment and support ring that are made of

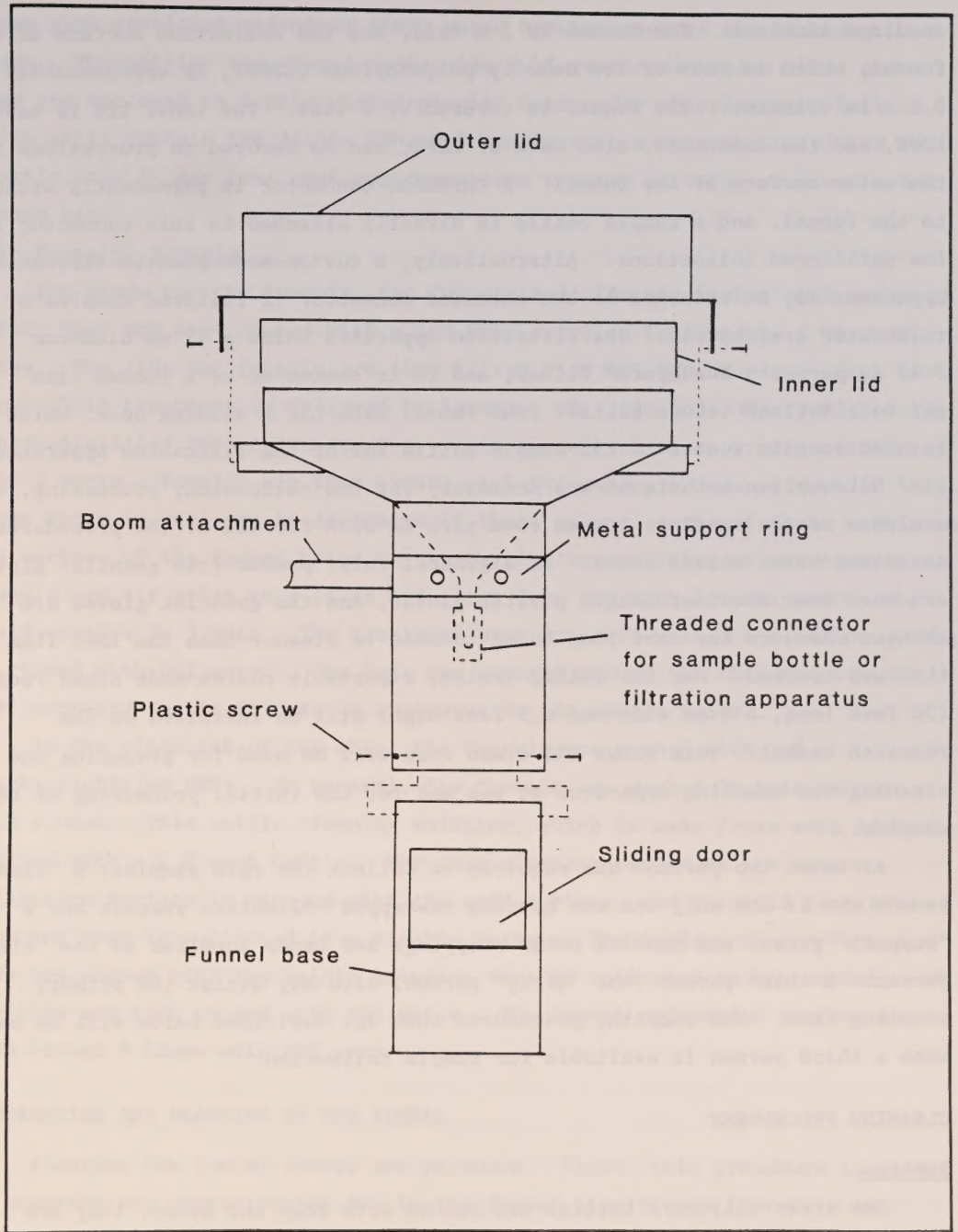


Figure 2. Rain Sampler for Shipboard Use.

anodized aluminum. The funnel is 1 m tall, and the collection surface of the funnel, which is made of low density polyethylene (LDPE), is approximately 0.5 m in diameter. The funnel is covered by 2 lids. The inner lid is made of LDPE, and the outer lid, also made of LDPE, can be secured to protrusions on the outer surface of the funnel. A threaded connector is permanently attached to the funnel, and a sample bottle is directly attached to this connector for the unfiltered collections. Alternatively, a custom-made plastic filtration apparatus may be attached to the threaded connector if filtered samples of rain water are desired. The filtration apparatus holds a 47 mm diameter 0.45 μ m porosity Nuclepore® filter, and it is connected to a vacuum line and to a Teflon® vacuum bottle. The funnel base has a sliding door, which is used to gain access to the sample bottle and/or the filtration apparatus.

Ultra-clean techniques are necessary for the collection, processing, and analyses of the samples. Clean room garb is worn for all of the procedures described below unless noted. As a general rule, powder-free gauntlet gloves are worn over shoulder length plastic gloves, and the gauntlet gloves are changed whenever the next item to be touched is cleaner than the last item that was touched. For the SEAREX cruise, a portable custom-made clean room (20 feet long, 8 feet wide and 8.5 feet high) will be installed on the research vessel. This class 100 clean room will be used for preparing and cleaning the sampling apparatus at sea and for the initial processing of the samples.

At least two persons are required to collect the rain samples: a "clean" person who is the only one who handles unwrapped collection vessels and a "support" person who handles outer wrappings and hands supplies to the "clean" person. A third person (the "dirty" person) also may assist the primary sampling team. The sampling procedures that are described below will be used when a third person is available for sample collection.

CLEANING PROCEDURES

Bottles

Two liter (2l) LDPE bottles are washed with soap and water; they are then leached for 6 or more days in each of the following solutions: 50% HCl, 50% HNO₃, 0.1% HNO₃, and fresh 0.1% HNO₃; the latter two solutions are prepared using HNO₃ doubly distilled in quartz. Bottles are rinsed three

times with distilled deionized (DDI) water between each of the leaching steps. The bottles are stored containing 0.1% quartz-distilled HNO_3 , and they are enclosed in 3 acid-washed plastic bags. For shipping, the bottles, which still contain the dilute HNO_3 and remain triple bagged, are placed in plastic tubs (6 per tub) that are themselves wrapped in large soap and water washed bags.

Rain Sampling Funnels

The bases for the funnels, the funnels and lids are washed with soap and water; they are next rinsed with a 10% HNO_3 solution followed by a DDI water rinse. The lids and funnels are then filled with 10% HNO_3 for one month or more. This treatment is followed by leaching the lids and funnels with 0.1% quartz-distilled HNO_3 solutions 3 or 4 times--each of these treatments lasts 2 or 3 weeks. Funnels are then rinsed with DDI water, and an aliquot of this rinse water is analyzed to determine if there is any source of trace metals on the surface of the funnel prior to the bagging and shipping of the funnels. Funnels are air dried in a class 100 clean lab, and they are shipped to the field wrapped in 3 bags. The two inner bags are acid-washed and the outer bag is rinsed with DDI water. The bags are secured around the threaded fitting that connects to the filtration apparatus or the sample bottle.

In the clean lab of the ship, the funnels are washed with 10% quartz-distilled HNO_3 . In general, the funnels are washed in this manner once a week. This acidic cleaning solution, which is made fresh each time, is applied with a 1 l wash bottle. For this cleaning procedure the entire collection surface is sprayed with the acid 5 times, and the acid from this cleaning step is collected in a plastic bucket. The insides of the funnel lids are rinsed with the acidic solution that is collected in the bucket, and the lids are then rinsed with DDI water. The funnel collection surface is also rinsed 5 times with DDI water.

PREPARATION AND BLANKING OF THE FUNNEL

Blanking the funnel serves two purposes. First, this procedure is used to quantify the contamination due to the funnel itself, and therefore the blank solution must mimic the sample as closely as possible. Second, the blanking procedure is used to monitor changes in the cleanliness of the funnel during the collection of sequential samples. If sequential samples are

collected, the blanking procedure should be performed before the first and the last collections at a minimum. Two persons are required to blank the funnel.

In the ship's clean lab, 1 bottle of DDI water MilliQ water (i.e., water that has passed through a MilliQ water purification system manufactured by Millipore, Bedford, MA) and 2 sample bottles (containing dilute HNO_3) are removed from their outer bags; the outer bags are saved for cleaning and reuse. These three bottles are placed on a clean surface, and the fastenings on the inner bags are loosened. The protective bags are removed from the funnel, and the outer lid of the funnel is removed and placed upside down on a clean surface. The inner lid is then removed and placed inside the outer lid in a "clam shell" fashion. The funnel base is removed and placed on a clean surface.

One sample bottle (S1) is removed from its inner bag, and the cap for the bottle is returned to the inner bag. The contents of the bottle are poured over the funnel, taking care to wet the entire collection surface. This liquid is discarded, so a waste receptacle must be placed under the funnel. Also the funnel must be held high enough above the waste container so that the funnel is not splashed by waste. The cap for the sample bottle (S1) is replaced, and the bottle is put back into its inner bag for later use in the blanking procedure.

For the next step of the blanking procedure, MilliQ or DDI water from the water bottle (W) is poured over the surface of the funnel, using the procedures described in the preceding paragraph; this material is also drained into the waste receptacle. The water bottle (W) is refilled, capped, and placed on a clean surface. The sample bottle (S1) from the prior cleaning step is attached to the threaded fitting of the funnel, and the MilliQ or DDI water from the refilled bottle (W) is then poured over the funnel, making sure that the entire collection surface is covered. The sample bottle (S1) is removed, capped, placed in 3 bags, and labeled as a blank. The contents of a second sample bottle (S2) are discarded, and that bottle is attached to the funnel in preparation for sample collection. The 2 funnel lids are put in place, and the funnel base is reattached. The funnel is placed in an acid-cleaned plastic bag, which is secured around the boom attachment.

COLLECTION PROCEDURES

Bow Procedure for Unfiltered Rain Samples.

The collection team brings the funnel and a plastic tub containing extra gloves and plastic bags to the bow of the ship prior to the rain event. The preparation for a rain collection takes about 30 minutes, so an early warning of an approaching rain storm from radar observers on the bridge is essential. The funnel should be blanked immediately before a rain collection, using the procedure described above. Two people [referred to henceforth as "C" ("clean" person) and "S" ("support" person)] are responsible for the rain collection, and they are dressed in plastic rain suits and wear shoulder length plastic gloves with several pairs of gauntlet gloves over the shoulder length gloves. A third person ("D," the "dirty" person) does not need to wear any special clothing or protection; he is in charge of handling the metal boom attachment and the mounting pins.

D attaches the funnel to the boom. S loosens the bag that encloses the funnel, removes the bag from the funnel, and holds it open. C removes the outer lid from the funnel, places the lid inside the bag held open by S, and changes gloves. Just before the rain event begins, C removes the inner lid and places it "clamshell" fashion inside the outer lid in the large bag held open by S. D orients the funnel and extends the boom to collect the rain with maximum efficiency.

Upon completion of the sample collection, D pulls in the boom. C and S put on new shoulder length gloves and gauntlet gloves. S then opens the bag containing the lids, and C takes the inner lid out of the bag and places it on the funnel. C changes gloves, and then he takes the outer lid out of the bag and places it over the inner lid on the funnel. S encloses the funnel in the large outer bag if it is still usable. If the outer bag is not clean, S will enclose the funnel in a new bag and secure the bag to the boom attachment. The funnel is then removed from the boom by D. C enters the anteroom, dresses in clean room garb, and then enters the clean room. S brings the funnel into the anteroom of the clean lab. In the anteroom, the bag enclosing the funnel is loosened by S, and C pulls the funnel into the clean lab. In the clean room, the sample bottle is removed, acidified, labeled, and triple bagged.

Filtered Rain Samples

In the clean lab of the ship, the funnel base is removed, and a filtration apparatus, with an acid-cleaned Nuclepore® filter inside, is secured to the threaded connector. The Teflon® vacuum bottle is attached to the filtration apparatus. Blanks for the filtered samples are obtained by pouring 2 l of DDI or MilliQ water over the entire collection surface of the funnel while a vacuum is applied to the filtration apparatus. The filtrate is transferred from the Teflon® vacuum bottle back into a 2 l sample bottle for storage as the blank. The filtration apparatus is removed from the threaded connector, and the filter from it is placed in an acid-washed petri dish. A clean filtration apparatus is attached to the threaded connector of the funnel, and the Teflon® vacuum bottle is rinsed 3 times with DDI water then reattached to the filtration apparatus.

The deployment of the funnel proceeds in a manner similar to the procedure described above for unfiltered rain samples, except that just after the removal of the inner lid by C, a vacuum line is attached to the filtration apparatus. C also checks inside the base to make sure that there is no air lock. It is therefore necessary that rain is actually falling before the inner lid is removed. After sampling is completed, C replaces the inner lid using fresh acid-washed gloved hands before he removes the vacuum line. Once the funnel is back in the clean room, the filtrate is poured into an acid-washed rain sample bottle and acidified, and the filter is placed in an acid-washed petri dish.

Storage of Samples

At the conclusion of the sample collections, approximately 1 ml of quartz-distilled HNO_3 is added to each liter of rain prior to freezing. Samples remain frozen until analysis. The filters from the rain filtering experiments are frozen in acid-washed petri dishes until analysis.

ACKNOWLEDGEMENTS

The rain sampling procedures described here are based on techniques developed by Clair Patterson and Dorothy Settle of the California Institute of Technology. Alan Hewitt also played an important role in the development of the clean techniques used for SEAREX. This research was supported by the National Science Foundation, under grants OCE77-13071, OCE77-13072, OCE81-11895, and OCE84-05605 as part of the SEAREX program.

LITERATURE CITED

- Arimoto, R., R. A. Duce, B. J. Ray, and C. K. Unni, Atmospheric trace elements at Enewetak Atoll: 2. Transport to the ocean by wet and dry deposition, J. Geophys. Res., **90**, 2391-2408, 1985.
- Buat-Menard, P., and R. Chesselet, Variable influence of the atmospheric flux on trace metal chemistry of suspended matter, Earth Planet. Sci. Lett., **42**, 399-411, 1979.
- Duce, R. A., G. L. Hoffman, B. J. Ray, I. S. Fletcher, P. R. Walsh, J. L. Fasching, S. R. Piotrowicz, E. J. Hoffman, J. M. Miller, and J. L. Heffter, Trace metals in the marine atmosphere: Sources and fluxes, in Marine Pollutant Transfer, edited by H. Windom and R.A. Duce, pp. 77-120, D.C. Heath, Lexington, Mass., 1976.
- Duce, R. A., R. Arimoto, B. J. Ray, C. K. Unni, and P. J. Harder, Atmospheric trace elements at Enewetak Atoll: 1, Concentrations, sources, and temporal variability, J. Geophys. Res., **88**, 5321-5342, 1983.
- Galloway, J. N., J. D. Thornton, S. A. Norton, H. L. Volchok, R. A. N. McLean, Trace metals in atmospheric deposition: A review and assessment, Atmos. Environ., **16**, 1677-1700, 1982.
- Maenhaut, W., M. Darzi, and J.W. Winchester, Seawater and nonseawater aerosol components in the marine atmosphere of Samoa, J. Geophys. Res., **86**, 3187-3193, 1981.
- Meinert, D. L., and J. W. Winchester, Chemical relationships in the North Atlantic marine aerosol, J. Geophys. Res., **82**, 1778-1782, 1977.
- Rahn, K. A., The chemical composition of the atmospheric aerosol, technical report, Graduate School of Oceanogr., Univ. of Rhode Island, Kingston, 1976.
- Settle, D. M., and Patterson, C. C., Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural leads to the North Pacific at Enewetak, J. Geophys. Res., **87**, 8857-8869, 1982.
- Zoller, W.H., E.S. Gladney, and R.A. Duce, Atmospheric concentrations and sources of trace metals at the south pole, Science, **183**, 198-200, 1974.

MEASUREMENTS OF TRACE METALS IN WET DEPOSITION AT RURAL SITES IN SWEDEN

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1. COLLECTION AND ANALYTICAL METHODOLOGIES

Trace metal concentrations are determined using graphite furnace atomic absorption spectroscopy (GFAAS). Procedures to avoid sample contamination are similar to those developed for the determination of trace metals in atmospheric precipitation from Antarctica and remote areas in the Pacific Ocean. A detailed description of these procedures are given in Ross (1984), briefly:

- A. All sampling equipment and storage bottles are washed in acids for one month.
- B. Samples are only handled in a metal-free clean room or in particle-free clean air bench.
- C. To avoid adsorption of metals onto container surfaces, samples and standards are acidified to a pH of 1 with super-pure concentrated HNO_3 .
- D. For the routine monitoring of trace metals in wet deposition, station managers are individually trained and are given detailed instructions in the placement and removal of the sample collectors.

2. ROUTINE MONITORING OF TRACE METALS IN ATMOSPHERIC PRECIPITATION

The routine monitoring of trace metals in atmospheric precipitation is part of the Swedish Environmental Protection Board (SNV) Program for Environmental Monitoring (PMK). The expressed purpose of our work is to determine the atmospheric wet deposition of Cd, Cu, Fe, Mn, Pb and Zn in

Sweden, and to eventually correlate metal concentrations in atmospheric precipitation to that in mosses (Hylocomium splendens and/or Pleurozium schreberi).

Wet deposition is collected on a monthly basis in bulk collectors (acid washed) at sixteen stations (Figure 1; dates when collection was started and 1984 volume weighted mean concentrations are given in the caption). At each station there are three collectors. Rain collectors are of funnel and bottle type and are constructed out of conventional polyethylene (CPE). The collectors are designed to hold a maximum of 125 mm of precipitation (500 ml sample). The collectors are placed 1 m from the ground and in open fields, at least 10 m from the nearest tree. The maximum distance between collectors does not exceed 40 m. Sampling locations are at least 500 m from the nearest road and 200 m from the nearest building.

The first stage of the monitoring program was to determine if the acid washing of collectors is necessary and to see how well we can collect samples and to analyze for trace metals. At 4 stations atmospheric precipitation was collected on a monthly basis in 5 acid washed bulk collectors and one sampler which had only been washed in de-ionized water (HD H₂O). The results from this work are given in Ross (1984) and (1986). With regards to the collection of wet deposition, it was found that:

- A. Contamination of samples in the field was random.
- B. The highest instances of contamination occurred for Mn.
- C. The monthly variation in metal concentrations in samples from the acid washed collectors was generally less than 5 percent.
- D. There was no systematic bias in metal concentrations due to the placing the collector at given location at a sampling site.

With regards to the acid washing of sampling equipment and labware it was found that:

- A. Sampling equipment and storage bottles should be acid washed.
- B. Many of the samples from the untreated collectors (i.e. collectors only

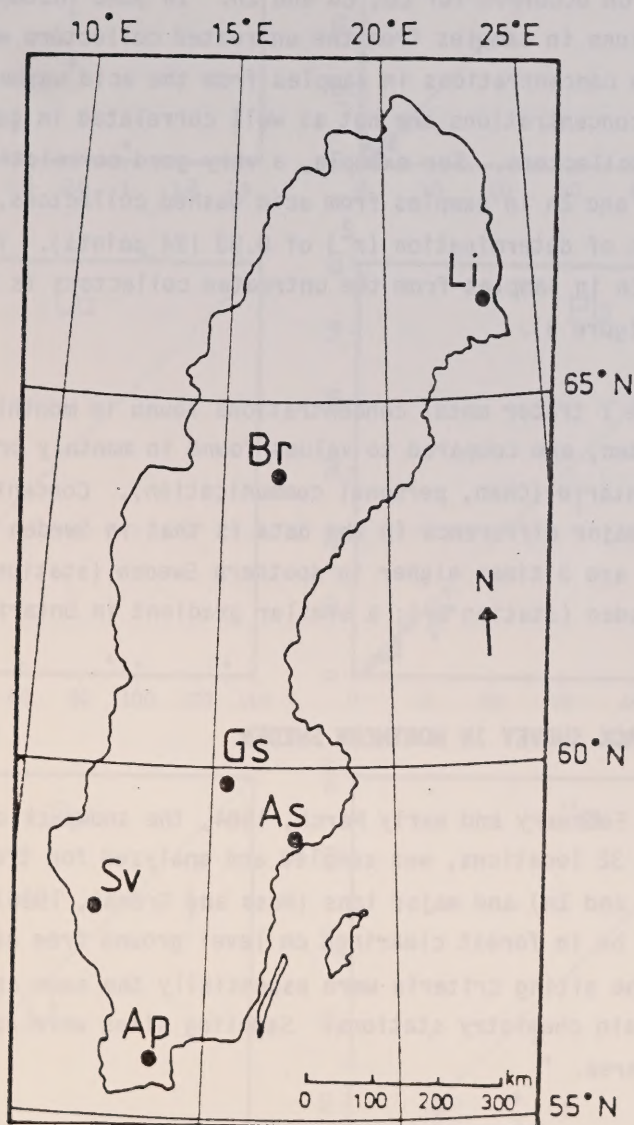


FIGURE 1. Locations where atmospheric precipitation is collected for heavy metal analysis.

Station	Starting Date	Station	Starting Date
AP - Arup	83/10/15	Gs - Grimsjö	85/06/27
AS - Aspvreten	83/10/04	Li - Liehittaja	84/06/02
Br - Bredkalen	84/05/03	Sv - Svartedalen	85/06/27

washed in HD H₂O) were contaminated, and the degree of contamination for each metal was different (Figure 2). The highest instances of contamination occurred for Cd, Cu and Zn. In some instances Cu concentrations in samples from the untreated collectors were 50 times higher than concentrations in samples from the acid washed collectors.

- C. Elemental concentrations are not as well correlated in samples from the untreated collectors. For example, a very good correlation is found between Cd and Zn in samples from acid washed collectors, yielding a coefficient of determination (r^2) of 0.93 (24 points). The correlation of Cd and Zn in samples from the untreated collectors is much poorer; r^2 is 0.34 (Figure 3).

In Table 1 tracer metal concentrations found in monthly precipitation samples in Sweden, are compared to values found in monthly precipitation samples from Ontario (Chan, personal communication). Concentrations are very similar. The major difference in the data is that in Sweden Cd, Cu, Pb and Zn concentrations are 3 times higher in southern Sweden (stations Ap and As) than in northern Sweden (station Br); a similar gradient in Ontario is only found for Pb.

3. 1984 SNOWPACK SURVEY IN NORTHERN SWEDEN

In late February and early March, 1984, the snowpack of northern Scandinavia at 32 locations, was sampled and analyzed for trace metals (Cd, Cu, Fe, Mn, Pb and Zn) and major ions (Ross and Granat, 1986). Sampling sites were chosen to be in forest clearings on level ground free of bushes and snowdrifts. The siting criteria were essentially the same as for the placement of rain chemistry stations. Sampling sites were approached by skiing to the area.

Snowpack samples were taken from a large trench which was dug with a plastic shovel. Before samples for trace metal analysis were taken, clean-room protective clothing (with hood) and shoulder length plastic gloves were put on. One of the walls of the trench was then cut back about 10cm with an acid washed plastic scraper. The total depth of the snowpack was sampled

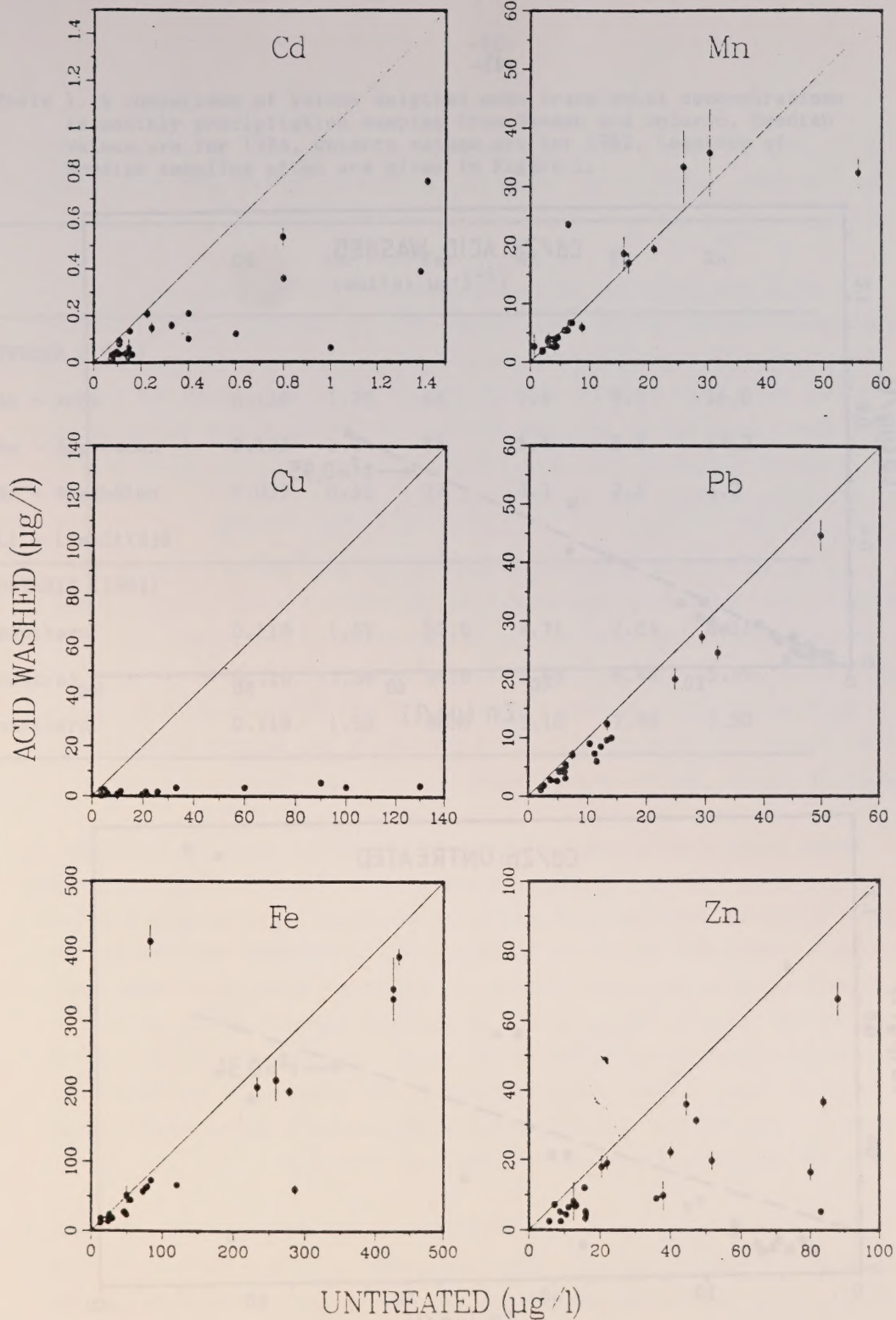


FIGURE 2. Trace metal concentrations in atmospheric precipitation collected in acid washed collectors versus metal concentrations in precipitation from untreated collectors. Collection and subsequent sample handling were the same for both types of precipitation. The error bars represent the standard deviation of metal concentrations from samples collected and stored in acid washed equipment.

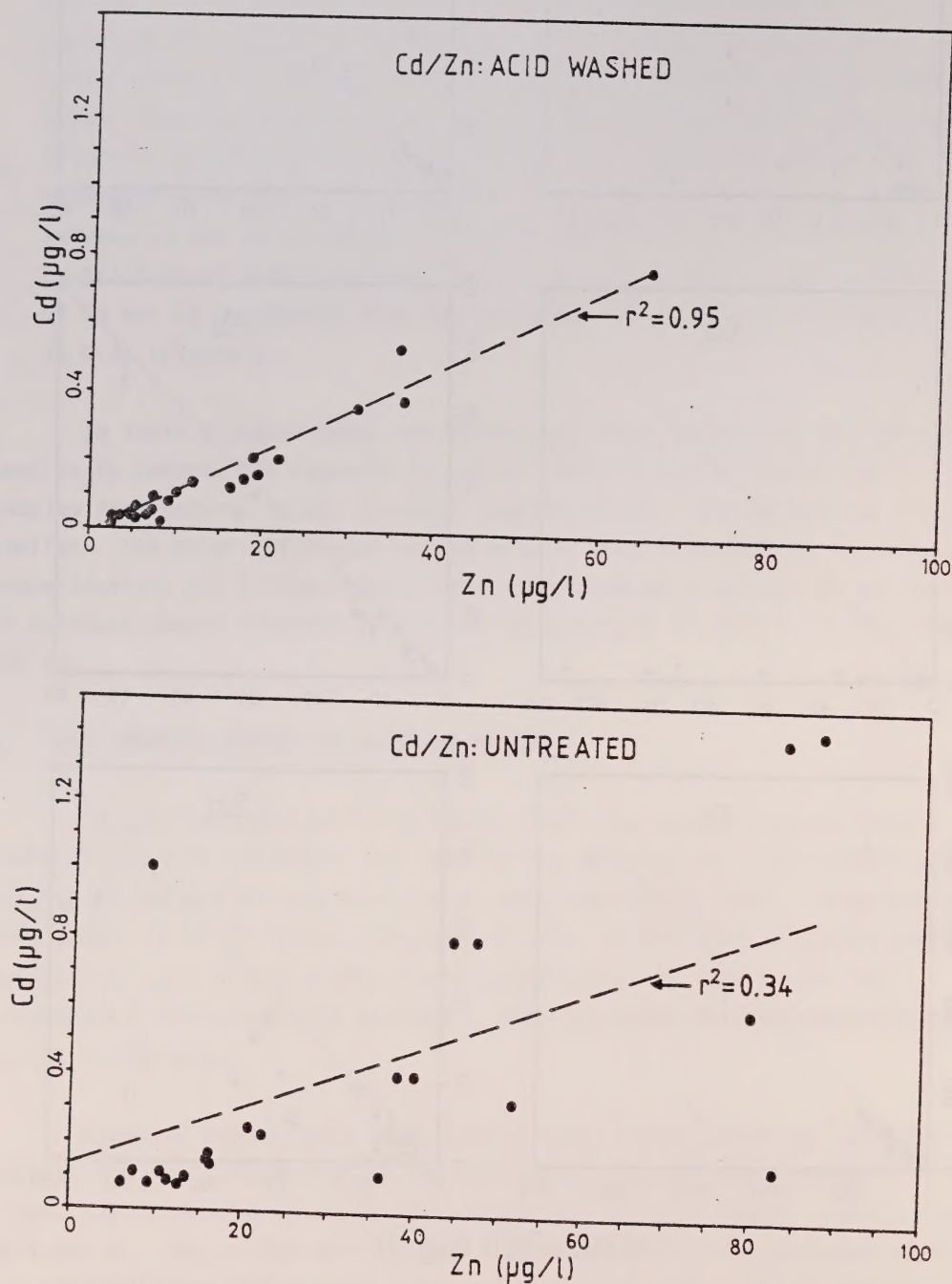


FIGURE 3. Plot of Cd to Zn in monthly atmospheric precipitation samples from acid washed and untread collectors. The dotted lines represent the least square fit to the data.

Table 1. A comparison of volume weighed mean trace metal concentrations in monthly precipitation samples from Sweden and Ontario. Swedish values are for 1984, Ontario values are for 1982. Location of Swedish sampling sites are given in Figure 1.

	Cd	Cu	Fe	Mn	Pb	Zn
	(units: $\mu\text{g}\cdot\text{l}^{-1}$)					
SWEDEN (1984)						
Ap - Arup	0.138	1.25	64	7.4	9.3	16.0
As - Aspvreten	0.133	1.04	55	5.6	8.2	14.2
Br - Bredkålen	0.035	0.38	27	3.2	2.5	4.2
Li - Liehittäjä						
ONTARIO (1982)						
southern	0.118	1.57	52.0	4.71	7.04	8.33
central	0.110	1.36	34.8	2.68	6.46	5.69
northern	0.118	1.58	40.4	3.10	2.98	5.50

by running the bottle along the cleared wall using the lip of the bottle as a scraper. At 27 of 36 locations, duplicate samples were taken 50-300 m away.

A comparison of major ion concentrations in the snowpack and monthly precipitation samples indicate that within 35%, the snowpack samples represent the volume weighted mean concentration of soluble ions in precipitation which fell during the winter months. The relatively small losses from the snowpack is more than likely due to that the sampling period was before the spring melt. Since little of the major ions have escaped from the snowpack, it is presumed that this would also be true for trace metals.

In Figure 4 trace metal concentration maps over northern Sweden are presented. For all metals, concentrations are highest along the Baltic coast and decrease towards the interior. With the exception of Fe, the concentration gradients along the coast are stronger than in the interior. The highest metal concentrations for Cd, Cu, Pb and Zn are found 5 km west of a large smelter (Ronnskarverket). This smelter is the largest point source of atmospheric Cd, Cu, Pb and Zn on Sweden.

Mean snowpack metal concentrations for different regions, delineated by the concentration isolines in Figure 4 are given in Table 1. These values are compared to volume weighted mean metal concentrations found in precipitation in southern Sweden for the period November 1983 to February 1984. Mn and Fe concentrations along the coast (regions I) are about three times lower than concentrations found in precipitation in southern Sweden. Pb and Zn concentrations are about a factor of two lower. Concentrations of Cd and Cu are about 30% lower. Metal concentrations in the snowpack in the interior (regions III and IV) are typically a factor of ten lower than concentrations found in precipitation in southern Sweden (see Table 2).

The minimum trace metal concentrations in the snowpack from the eastern Canadian shield (Barrie and Vet, 1984) correspond to values found in regions II or III. With respect to other trace metal concentrations reported in the literature for rural regions, summarized by Galloway et al (1982), metal

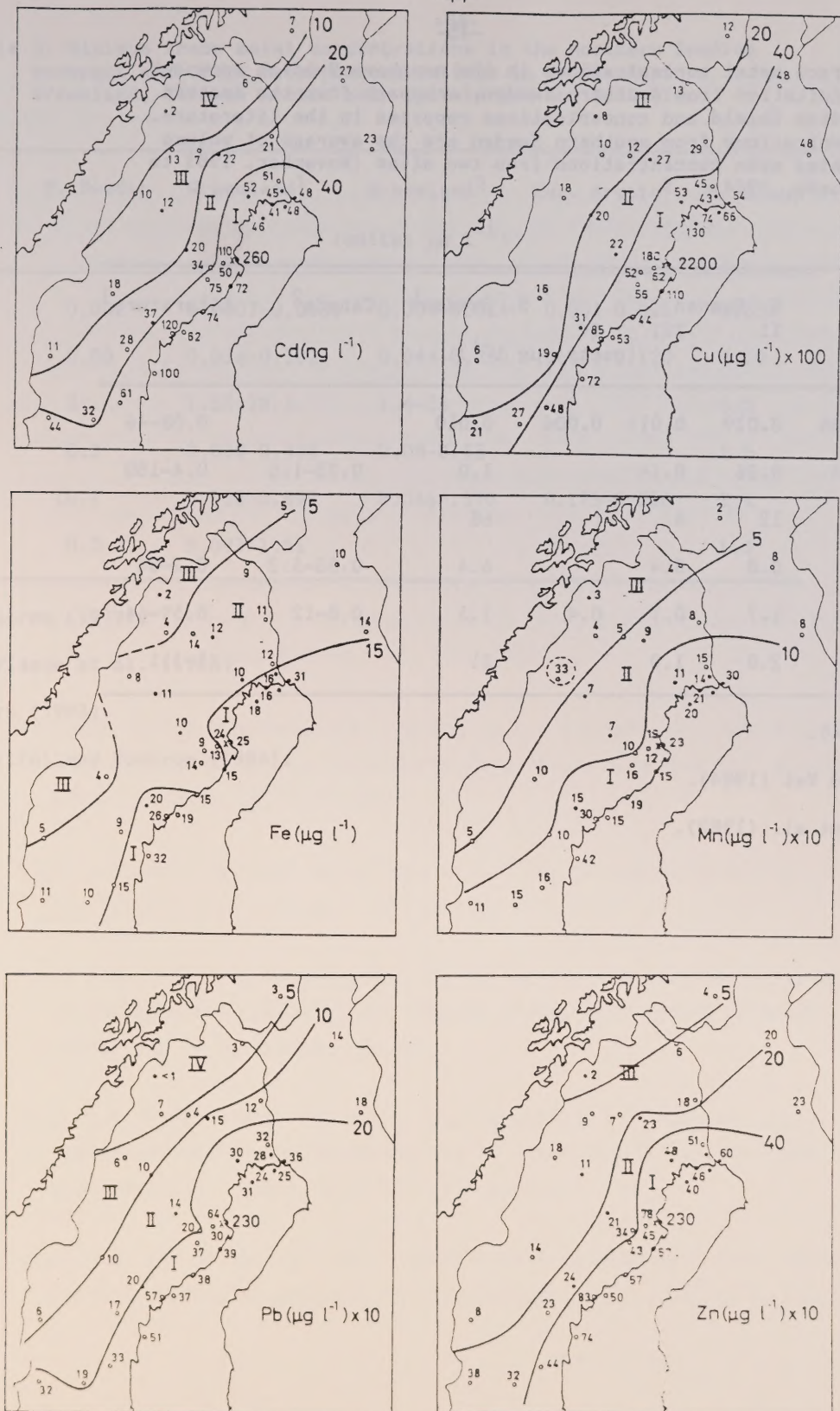


FIGURE 4. Trace metal concentrations found in the 1984 northern Sweden snowpack.

Table 2. Trace metal concentrations in the northern Swedish snowpack, precipitation from southern Sweden, snowpack from the eastern Canadian Shield and concentrations reported in the literature. Concentrations from southern Sweden are the average of volume weighted mean concentrations from two sites (November, 1983 to February, 1984).

I	N. Sweden		S. Sweden ¹		Canada ²	Literature ³
	II	III	IV			
	(units: $\mu\text{g l}^{-1}$)					
Cd	0.066	0.029	0.014	0.006	0.010	0.08-46
Cu	0.74	0.26	0.14		1.0	0.25-1.6
Fe	21	12	4		68	
Mn	1.8	0.8	0.4		6.4	0.55-5.2
Pb	3.7	1.7	0.7	0.4	7.3	0.8-12
Zn	5.5	2.8	1.0		11	<1-311

¹Ross (1984).

²Barrie and Vet (1984).

³Galloway et al. (1982).

Table 3. Minimum trace metal concentrations in the northern Swedish snowpack and trace metal concentrations in snowpacks from Greenland, European Arctic near Spitsbergen and Mont Blanc.

	N. Sweden	Greenland ¹	Greenland ²	Eur. Arctic ²	M. Blanc ³
	(units: $\mu\text{g l}^{-1}$)				
Cd	0.002	0.0007-0.0085	0.004-0.024	0.003-0.006	0.054
Cu	0.08	0.036-0.102	0.044-0.250	0.080-0.120	0.18
Fe	2	1.53-28.3	1.4-23		6.3
Mn	0.3	0.030-0.438	0.08-0.55		1.3
Pb	<0.1	0.128-0.899	0.046-.390	0.173-0.226	2.4
Zn	0.2	0.097-1.51			1.3

¹Boutron (1979).

²Davidson et al. (1985)

³Mart (1983).

⁴Batifol and Boutron (1984).

concentrations in northern Sweden are substantially lower (see Table 1). Ross (1986) has suggested that a portion of these high metal concentrations may be attributed to sample contamination.

Lowest concentrations for all metals are found at sites in the Swedish mountains, in Northwestern Sweden near the Norwegian border. Minimum concentrations in the northern Swedish snowpack are comparable to concentrations found in accumulated snow in Greenland (Boutron, 1979; Davidson, 1985) and in the European Arctic near Spitsbergen (Mart, 1983). Batifol and Boutron (1984) have measured trace metals in high altitude snow at Mont Blanc, in the French Alps. Minimum concentrations in northern Sweden are about a factor of 2-25 lower (see Table 3).

References

- Barrie, L.A. and Vet, R.J. 1984. The concentration and deposition of acidity, major ions and trace metals in the snowpack of the eastern Canadian Shield during the winter of 1980-1981. *Atmos. Environ.* 18, 1459-1469.
- Batifol, F.M. and Boutron, C.F. 1984. Atmospheric heavy metals in high altitude surface snow from Mont Blanc, French Alps. *Atmos. Environ.* 18, 2507-2515.
- Boutron, C. 1979. Trace element content of Greenland snows along an east-west transect. *Geochim. Cosmochim. Acta* 43, 1253-1258.
- Davidson, C.O., Santhanam, S., Fortmann, R.C. and Olson, M.P. 1985. Atmospheric transport and deposition of trace elements onto the Greenland ice sheet. *Atmos. Environ.* 19, 2065-2082.
- Galloway, N.J., Thornton, J.D., Norton, S.A., Volchok, H.L. and McLean, R.A.N. 1982. Trace metals in atmospheric deposition: a review and assessment. *Atmos. Environ.* 16, 1677-1700.
- Mart, L. 1983. Seasonal variations of Cd, Pb, Cu and Ni levels in snow from the eastern Arctic Ocean. *Tellus* 35B, 131-141.
- Ross, H.B. 1984. Methodology for the Collection and Analysis of Trace Metals in Atmospheric Precipitation. Report CM-67. Department of Meteorology, University of Stockholm. 35 pp.
- Ross, H.B. 1986. Technical Note: The importance of reducing sample contamination in routine monitoring of trace metals in atmospheric precipitation. *Atmos. Environ.* (in press).
- Ross, H.B. and Granat, L. 1986. Deposition of atmospheric trace metals in northern Sweden as measured in the snowpack; 1984. *Tellus B.* (in press).

SUMMARY of 1984 EMEP WORKSHOP on HEAVY METALS
and ITS MAJOR CONCLUSIONS*

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ENVIRONMENT CANADA

Introduction

From August 27-29, 1984, I had the distinct pleasure of attending--as the Canadian delegate--the EMEP Workshop on Heavy Metals held at the Norwegian Institute for Air Research (NILU) located in Lillestrom, near Oslo. The European Monitoring and Evaluation Programme (EMEP) is a collaborative venture for monitoring and assessing the long-range transport of air pollutants in Europe. It is organized under the Economic Commission for Europe (ECE)--a United Nations body. This programme functions in close co-operation with the World Meteorological Organization (WMO) and the U.N. Environment Programme (UNEP). The EMEP organizational structure is shown in Figure 1.

Background to the Workshop

At its seventh session (held in Geneva from November 10-11, 1983), the EMEP Steering Body received a proposal from the delegation of the Federal Republic of Germany (F.R.G.) regarding "Monitoring within EMEP of Certain Further Pollutants." At that time, substances which already were being monitored regularly within the established protocol of the European Monitoring and Evaluation Programme included the following: sulphur dioxide (SO_2) ; suspended particulate matter and related compounds (TSP); and major components of precipitation.

In addition to suggestions for additional measurements pertaining to nitrogen oxides and ozone in ambient air, the F.R.G. proposal specifically called for the inclusion of measurements for the heavy metals lead (Pb) and cadmium (Cd) within the EMEP framework. The suggestions contained in the proposal tabled by the Federal Republic of Germany at the Geneva meeting

* Presented at "Workshop on the Measurement of Metals in Precipitation",
Atmospheric Environment Service, Downsview, Ontario; January 29-30, 1986.

EMEP

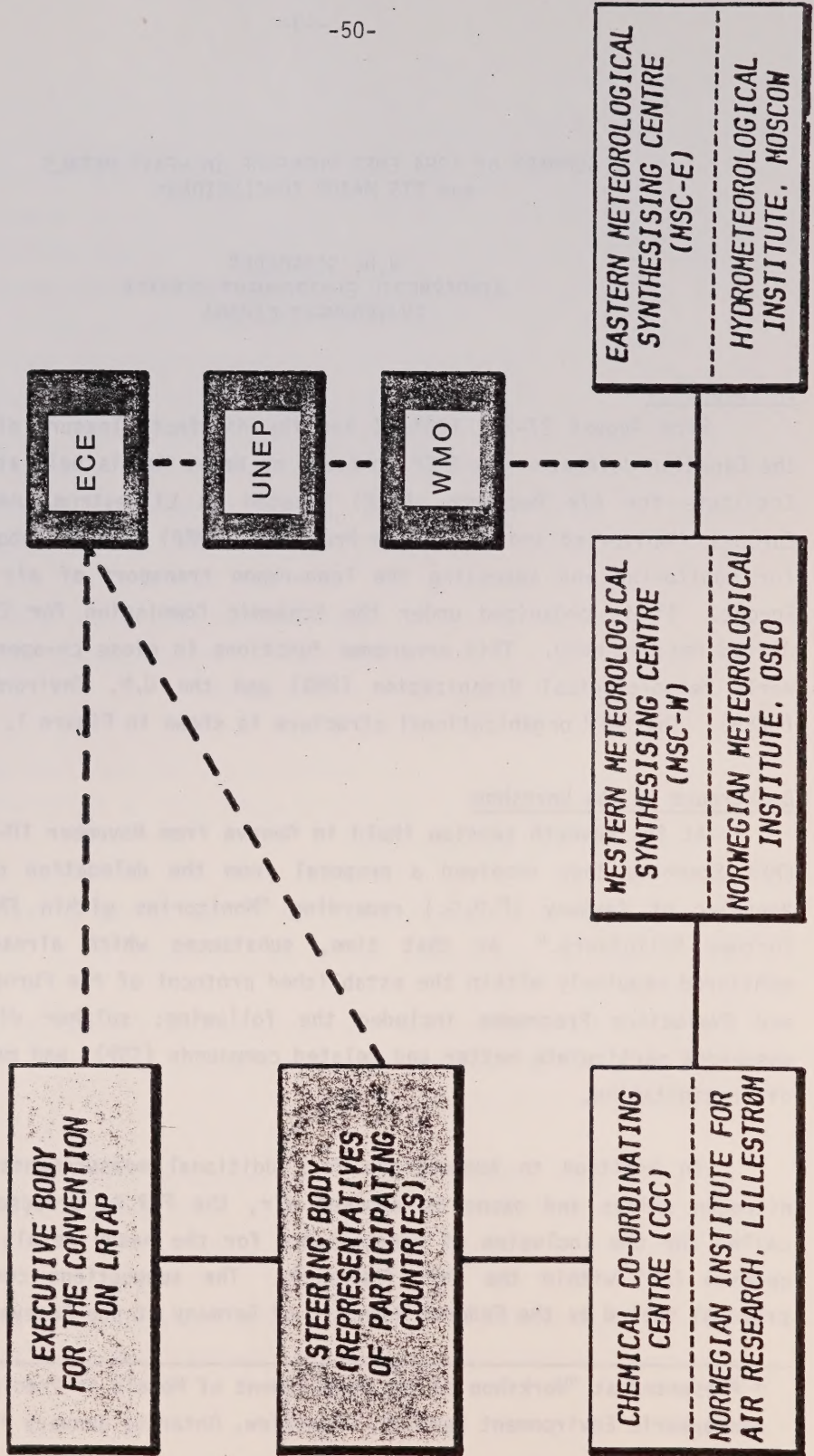


FIGURE 1. THE EMEP (EUROPEAN MONITORING AND EVALUATION PROGRAMME) ORGANIZATIONAL STRUCTURE.

arose out of a growing concern over a new phenomenon observed in recent years in a number of European countries. This phenomenon, termed "neuartige Waldschaden" by the Germans, is characterized by a dramatic progression of disease and death of trees in large, yet separate, areas of forests. In the F.R.G., for example, the areas being impacted are apparently spreading rapidly. In the early days of the development of this phenomenon, discussions about possible causes were controversial and overheated. At the present time, a consensus seems to be developing that air pollution is the dominant cause, although other factors such as climatic events, disease and forestry management practices may be of importance also and cannot yet be ruled out. Because damages are occurring in regions remote from heavily urbanized and industrialized areas, large-scale air pollution is thought to play an important role. Heavy metals are implicated in this alarming damage to the forests on the basis of their known toxic effects, their mobility and persistence in the biosphere and their propensity to accumulate in the environment, particularly in soils.

In view of the proposal received from the delegation of the F.R.G., the Steering Body of EMEP at its seventh session decided that the Chemical Coordinating Centre (CCC) should organize a workshop to discuss technical aspects related to environmental monitoring of heavy metals. Consequently, an international workshop with about 35 participants was convened at the Norwegian Institute for Air Research in Lillestrom, approximately 20 km north-east of Oslo, for a period of 2 1/2 days in August 1984. The workshop agenda is provided as Appendix I.

Technical Program for EMEP Workshop

The workshop was organized so as to comprise a combination of plenary and working group sessions. Welcoming remarks and introductory observations and comments were delivered by Dr. B. Ottar, Director of NILU. He was followed by an invited speaker--Professor G. Tyler from the University of Lund, Sweden--who presented a keynote lecture on the present state of knowledge concerning the effects of heavy metals on humans and the environment. Other topics addressed in plenary lectures at this workshop are summarized in Table I. Some of the more important questions posed and discussed by workshop attendees during plenary and/or working sessions are given in Table II.

Table I. Some topics addressed in plenary lectures at the EMEP Workshop

- Measurement (sampling and analysis) of metals associated with airborne particulate matter (aerosols) and in precipitation;
- Analytical quality control and use of certified reference materials;
- Anthropogenic emissions of trace elements in Europe and their long-range aerial transport;
- Sampling and analysis of atmospheric mercury and Scandinavian data from measurements in air and natural waters;
- Use of mosses in heavy metal deposition studies;
- Statistical analysis (including multivariate techniques) of monitoring data;
- Current activities in member countries relative to heavy metal measurements;
- Analytical methods for determining low (i.e., background) concentrations of heavy metals in air and/or precipitation;
- Equipment and materials/supplies suitable for air and precipitation sampling.

TABLE II. Some important questions discussed by workshop participants in plenary and/or working sessions at the EMEP workshop

- Which questions should the EMEP Programme on heavy metals be designed to answer?
- Which chemical elements should be included in the programme?
- What sample medium and what type of sampler should be chosen?
- What should the sampling frequency be?
- Which analytical methods should be recommended?
- What actions should be taken to ensure high quality data?
- Should chemical analyses be carried out in one central lab or in several national labs?
- How should the collected data be reported and presented within the EMEP framework?
- What about further data evaluation and interpretation?

Conclusions and Recommendations from EMEP Workshop

Heavy metals constitute a potential hazard since they may accumulate in the environment. Presentations to the workshop illustrated the atmospheric long-range transport of several heavy metals. The workshop attendees, therefore, agreed on the desirability of obtaining further information on the atmospheric concentrations and deposition of heavy metals over Europe. The workshop participants expressed the view that a programme on heavy metals should complement measurement activities related to acidic substances (or their precursors) and photochemical oxidants.

As a first step, the EMEP Centres should collect available information on:

- 1) Emissions of heavy metals
- 2) Their concentrations in air and precipitation
- 3) Sampling and analytical methodology
- 4) Chemical and physical characteristics of heavy metals and their compounds.

At the same time, an initial study lasting two years should be commenced. Towards the end of this study, the need for a longer term programme should be assessed. This initial study should consist of measurements of heavy metals in airborne particulate matter and possibly wet deposition. The workshop also noted that moss studies could yield useful information on deposition patterns. Sampling and chemical analyses should be undertaken by laboratories in the participating countries. Due to the difficulties inherent in sampling and chemical analyses, stringent quality controls measures, such as laboratory intercomparisons, would need to be implemented.

As many elements as possible should be included in the programme to assess the long-range transport of heavy metals through the atmosphere. Due to the toxic effects of cadmium (Cd), lead (Pb), zinc (Zn) and arsenic (As), these elements should be included in any heavy metal measurement activity. Further elements, which may be of interest because of their toxicity, or as tracers for certain emissions, include the following: vanadium (V), nickel (Ni), copper (Cu), antimony (Sb), selenium (Se), and manganese (Mn). Also, in order to aid data interpretation, one or more elements typical of the earth's

crust--silicon (Si), aluminum (Al), iron (Fe), or titanium (Ti)--should be included. Mercury (Hg) was recognized as an important element both in terms of environmental and human health concerns. It provides a good example of how important it is to have information on the individual chemical forms (species) to allow further evaluation. Its environmental chemistry and reliable determination (at least on a routine basis) is so complicated, however, that inclusion of Hg in the proposed programme would be premature at present.

The workshop participants felt that the Chemical Co-ordinating Centre should be responsible for the co-ordination of this programme. Its responsibilities should include data collection and quality control/assurance procedures. The results of this enhanced measurement programme, together with emission inventories, will be useful for evaluation and further development of various LRTAP models at the Meteorological Synthesizing Centres of EMEP.

EMEP Workshop Agenda

Appendix I

Monday 27th August

B. Ottar (Norway, CCC)

Opening of the meeting - objectives.

G. Tyler (Invited speaker, Sweden, University of Lund)

Heavy metals and the environment.

H.B. Ross (Sweden, University of Stockholm)

Determination of trace metals in atmospheric precipitation - experimental methodology.

J. Muller (Germany, F.R., Umweltbundesamt Frankfurt)

Measurement of heavy metals in airborne particulate matter, dry and wet deposition.

J.E. Hanssen (Norway, CCC)

Available methods for sampling and analysis of metals in aerosols and precipitation.

Tuesday 28th August

R.M. Parr (Austria, International Atomic Energy Agency)

IAEA Programmes relating to trace elements in air pollution.

B. Moldan (Czechoslovakia, University of Prague)

Experience with the analysis of trace constituents of air and atmospheric deposition in Czechoslovakia.

R. Hillamo (Finland, Finnish Meteorological Institute)

Fine particle aerosols in Southern Finland.

S. Cerquiglini Monteriolo, M. Bertolaccini, F.D. Innocenzio, P. Gucci, G. Viviano, G. Ziemacki (Italy, Istituto Superiore di Sanita).

ISS research activities on airborne heavy metals in urban industrial and rural areas.

J. Pacyna (Norway, NILU)

Anthropogenic emissions of atmospheric trace elements in Europe.

A. Semb (Norway, NILU)

Long range transport of trace elements.

C. Brosset (Sweden, IVL)

Swedish data concerning mercury in air and natural waters.

W.H. Schroeder (Canada, Environment Canada)

Sampling and analysis of mercury in ambient air.

E. Steinnes (Norway, University of Trondheim)

Use of mosses in heavy metal deposition studies.

K. Kemp (Denmark, Miljøstyrelsens luftforurenings laboratorium)

Multivariate analysis of sulphur dioxide and metals measured at the Danish EMEP stations.

A METHOD FOR THE COLLECTION, HANDLING AND ANALYSIS
OF TRACE METALS IN PRECIPITATION

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ABSTRACT

Wet deposition is an important environmental pathway for trace metals. This is of concern due to the toxic effects of many metals and the potential for contamination of rivers, lakes, streams and oceans. Trace metal sampling and analysis requires extreme care. A method is described for the automatic collection, proper handling and accurate analysis of trace metals in precipitation. The method has been developed and proven in both rural coastal (Lewes, Delaware, USA) and semi-remote (Bermuda) marine environments, but should be generally applicable.

The collection device is a commercially modified automatic HASL-ACM collector with polyethylene bag liners in the collecting buckets. Stringent acid washing, deployment, and blanking protocols are necessary to insure accurate samples. The freshly collected event samples are post-acidified below pH2 with ultra-clean HCl to insure desorption and preservation of the sample. The accuracy of the collection methods have been verified by duplicate manual collections simultaneously deployed over a year. The total (dissolved and particulate) sample is quantitatively analyzed by heated graphite atomization in an atomic absorption spectrophotometer.

Introduction

There is considerable evidence that atmospheric transport and deposition are important processes in the global cycling of trace metals. In many marine environments, the inventory and flux

of trace metals observed in the water column (1,2), suspended particulate (3,4), and sediments (5) are directly attributable to atmospheric flux. In terrestrial areas, elevated concentrations of trace metals in lakes, streams, soils and plants are often the result of atmospheric deposition (6-10). Many potentially toxic metals, such as Zn, Cd and Pb, are emitted into the atmosphere by heavy industry, automobiles, fossil fuel combustion and smelters at rates that far outweigh natural contributions (5,11,12). Numerous studies have shown most trace metal emissions are efficiently washed out of the atmosphere and returned to earth by precipitation. In fact, some samples of wet atmospheric deposition have been found to have concentrations of Pb, Hg, Cu, Zn and Cd that exceed levels toxic to aquatic organisms (13) and have been linked to deterioration in forest productivity (14). Furthermore, numerous studies [as reviewed by Graedel and Weschler (15)] have identified transition metals as important redox catalysts within atmospheric aerosol and aqueous phases, particularly with respect to the SO_2/SO_4 system.

To date, considerable effort has gone into the collection and measurement of trace metal aerosols in the atmosphere. Indirect estimates of the atmospheric deposition of trace metals based on ambient aerosol concentrations are difficult due to uncertainties in particle settling rates (dry deposition velocities) and precipitation scavenging efficiencies (washout factors). Attempts to measure dry deposition directly are hindered by the inability to reliably capture a representative sample.

Methods for the reliable and accurate collection of precipitation for pH and major ions have been developed (16). However, the accurate measurement of trace metal concentrations in wet deposition is a far more difficult undertaking, requiring a protocol more rigorous than ones used for acid precipitation studies. The major difficulties include: the contamination and/or adsorption of trace metals in aqueous samples during collection

and storage, difficulties in accurately analyzing sub-microgram concentrations, and the exclusion of dry deposition.

A survey of the major studies which have attempted to quantify the concentration of trace metals in precipitation (13), show a variety of sampling and analysis procedures have been utilized, many of which fail to address some or all of the aforementioned problems. Other studies (17,18), cognizant of the necessary precautions, employ custom-built automated samplers, which are potentially cost prohibitive or not readily available for use in a network format. Other investigators (2,6,11,19), have used manually deployed funnel and bottle-style collectors, which are inexpensive, non-contaminating, easily cleaned and deployed. However, such labor-intensive methods are not practical for long-term monitoring efforts, are inefficient for the capture of snow, and often result in a higher frequency of partially or completely missed events. Finally, most studies fail to report appropriate laboratory and field blanks. Thus, it is difficult to assess the accuracy and reliability of these methods.

By way of illustration, Table I presents a comparison of some previously published results on trace metals in precipitation at rural locations as reviewed by Galloway et.al. (13), and those collected at a semi-remote location along the middle Atlantic coast (Lewes, Delaware) and published elsewhere (20) which utilize the protocol to be described here. This comparison (Table I), reveals a large range in the reported trace metal concentrations in precipitation, suggesting that the earlier studies had orders of magnitude contamination resulting from such problems as improper collector materials, siting, handling, preservation, and analysis. Many of these efforts sought to simply analyze aliquots from samples collected primarily for major ion composition. We found such an approach unacceptable in that comparative studies resulted in either contamination or adsorption of trace metals. Thus, we proceeded to develop an accurate technique for the collection,

TABLE I

Comparative Concentrations of Trace Metals
in Precipitation

<u>Metal</u>	<u>Literature Range¹ (µg/l)</u>	<u>No. of References</u>	<u>Median¹ µg/l</u>	<u>Lewes Ave.² µg/l</u>
Cd	0.08-46	(23)	0.5	0.18
Cu	0.4 -150	(19)	5.4	0.68
Pb	0.59-64	(32)	12	3.02
Mn	0.2 -84	(28)	5.7	1.4
Ni	0.6 -48	(15)	2.4	0.79
V	0.13-23	(6)	9	0.7
Zn	<1 -311	(32)	36	6.4

¹From Galloway et.al. (13); values reported for rural locations (Tables 4 and 5).

²From Church et.al. (20).

handling, and analysis of trace metals in precipitation described in this paper.

We will first describe, in detail, our method which is the consequence of experimentation and development in collecting trace metal precipitation samples for over three years. Then, by examining the data from collections at two contrasting sample locations, demonstrate the accuracy and applicability of our technique.

PROCEDURE

Sampling Location

In general, the collector siting criteria applicable to any precipitation chemistry study (21) should be utilized. The sampling site should be sufficiently remote from local sources of trace metals and other atmospheric debris. These sources include automobile traffic, cultivated fields, smoke stacks, air ducts, etc. The site should also be well removed from any metal supports, wires or poles. Additional considerations are site security, accessibility, electric power availability and potential for land use changes. For our study, sampling is carried out at two collection sites: the middle Atlantic coast (Lewes, Delaware, USA) and at the mid-western Atlantic island of Bermuda. A detailed description of the two sites has been reported by Church et.al. (20). The collections were made as part of the Western Atlantic Ocean Experiment (WATOX) sponsored by NOAA to assess the transport and deposition of emission components from North America to the Atlantic Ocean.

Cleaning Procedures

The levels of trace metals in precipitation are relatively low (Table I), thus, sampling equipment, storage bottles and acids must be scrupulously cleaned. Materials made of polyethylene

(CPE) and polypropylene are exclusively used for sampling, storage and laboratory manipulation. The cleaning procedure, outlined in Table II, involves several sequential washings and rinsings in soapy water, acetone, HCl and HNO₃ acids. Rinse water is provided from a Millipore Milli-RO/Milli-Q (Millipore Corp., Bedford, MA) system (MQ-H₂O) or distilled/deionized is used (DDW). For laboratory analyses, distilled deionized water is further cleaned by sub-boiling in an all quartz stills (henceforth referred to as Q-H₂O). Likewise reagent grade hydrochloric and nitric acids are cleaned in an identical manner (Q-HCl and Q-HNO₃).

Collection Materials

Event samples for trace metal analysis are collected using a modified AeroChem Metrics (ACM) automatic collector (Model #301 AeroChem Metrics, Inc, Bushnell, Florida), factory equipped with all plastic components in the closing lid, displacement of the sensor grid, and teflon coating on the lid support arms. The modified ACM collector is well suited to the collection of wet deposition, as it is automated, dependable, widely used in meteorological studies, relatively inexpensive and commercially available. Its automated function is essential for unattended sampling in remote locations or for long-term monitoring.

Of equal importance, the collector and its sample receptacle must be non-contaminating. In laboratory experiments, the standard white plastic ACM buckets were found, even after extensive acid cleaning, to contaminate acidified Q-water (pH2 with Q-HCl) from less than 1 µg/l to 27 µg/l Zn, 16 µg/l Cu, 11 µg/l Pb and 10.5 µg/l Mn after 20 hours of soaking. When similar experiments were repeated with the ACM bucket lined with several types of polyethylene bag liners, insignificant (<10%) contamination of the Q-water occurred after 30 hours of soaking. Likewise, comparative field experiments using: extensively acid cleaned ACM buckets, ACM buckets cleaned for major ion sampling (16,22); and ACM buckets

TABLE II

Cleaning procedure for plasticware utilized for the collection, storage and analysis of trace metals in precipitation.

1. Wash with soapy deionized water (Fisher versa-clean or similar liquid).
2. Rinse 3 times with deionized water.
3. Shake off excess water.
4. Soak inside with spex grade acetone for 10 minutes.
5. Shake off excess acetone.
6. Swirl inside with concentrated reagent A.C.S. HCl.
7. Rinse 3 times with distilled water.
8. Swirl inside with concentrated reagent A.C.S. HNO₃.
9. Rinse 3 times with distilled water.
10. Place in warm 6N reagent A.C.S. HNO₃ bath for 2-3 days.
11. Transfer to 2N HNO₃ bath and soak for 2-3 days.
12. Rinse outside of container with deionized water.
13. Rinse inside of container 3 times with double distilled water.
14. Rinse inside of container with Q-H₂O.
15. Dry in a filtered air clean bench or hood.
16. Place and seal in a polyethylene zipper bag.

lined with polyethylene bags, resulted in contamination of trace metals by unlined buckets. In this study, 4 mil (0.004 inch) 10"x8"x24" gussetted polyethylene bags, rigorously washed according to (Table II), (Associated Bag Co., Milwaukee, Wisconsin, #47-6-51C) are used to line the ACM bucket. This commercially available thick walled bag was found to be non-contaminating and holds up to rigorous acid cleaning. As an independent comparison with the automated collector, a manual bulk (MB) sampler should be used for a minimum subset of the events. Our MB sampler is a polyethylene funnel, screw-fitted onto a two liter polyethylene bottle of the same design employed by the Global Precipitation Chemistry Project (6).

The use of bag liners is particularly advantageous in instances where more than one collection site is supplied by a centralized laboratory. We have found that the distribution of disposable acid washed bags to remote sites is considerably easier and less expensive than a two-way exchange involving buckets or funnels and bottles.

Deployment

An acid cleaned bag liner is installed into the ACM bucket within a clean bench. To minimize contamination, personnel should wear clean lab coats, polyethylene disposable gloves and hats for this and all other procedures. The top of the bag is folded over the lip of the ACM bucket and as much air as possible is pushed out from under the bag, which prevents the bag from blowing out in high winds. Once in place, 250-500 mls of Q-H₂O is rinsed down the sides of the bag liner, the bucket inverted, shaken dry, and doubly sealed in large plastic bags for transport to the collection site. At the site, the bucket with bag liner is removed from the transport bags, rinsed 3 times with MQ-H₂O, swirled, inverted, shaken dry, and installed into the ACM. In the event of an extended dry period (week to ten days), after periods of fog, dew or high

wind causing lid openings, or in instances where the amount of precipitation collected is insufficient for analysis, a new bucket and liner should be installed.

Similarly, the MB collector is acid cleaned, rinsed in the laboratory, and doubly sealed in large plastic bags for transport to the collection site. At the site, the MB collector is deployed on a plastic pole a few meters above the ground, yet sufficiently isolated from the ACM collector. The MB collector should be uncovered only during the precipitation event. After the event has ended, the samples are retrieved and inspected for the presence of any local debris (insects, bird droppings, plant detritus, etc.). If such debris is present, the samples are noted as suspect. The sample containers are tightly covered with clean plastic bags. The samplers are then placed in a second bag and transported upright to a laboratory clean bench or clean room.

Sample preservation

A major problem with any natural aqueous trace metal sample is the loss of metal from solution due to adsorption during collection and storage. Therefore, acidification to $\leq \text{pH} 2$ is routinely used for the preservation of such trace metal samples. Generally, acidification to 0.2% (v/v) with Q-HCl or Q-HNO₃ immediately after collection is sufficient to adjust the sample pH to less than 2 and prevent adsorption. Because of the sampling of wet deposition can require hours to days to complete, adsorption must be prevented at the onset or reversed after completion of sampling. Thus, we tested two approaches for the preservation of wet deposition samples: (1) to prevent adsorption, pre-acidification of the sampler before the event, and (2) to desorb any trace metals by post-acidification.

To test the two techniques, pairs of lined ACM buckets were simultaneously deployed side-by-side at the beginning of 7 different

precipitation event (2 were conducted at Bermuda and 5 at Lewes).

In each case, one of each sample pair was pre-acidified by adding 5 mls of a 50% Q-HCl solution before the event, and the second post-acidified to 0.2% v/v Q-HCl after the end of the event. A desorption period of at least six, but less than 24 hours was allowed prior to transferring to storage bottles.

A comparison of concentrations obtained from the pre- and post-acidified ACM collectors were within 20% agreement with an average difference of 7.5%, suggesting post-acidification is similar to pre-acidification in quantitatively reversing any adsorption which may occur during sampling. The exception is Cd, where the mean concentration is 32% greater in the pre-acidified ACM samples. We attribute this to contamination due to the prolonged exposure of the sampling equipment to the concentrated acid pre-spike which has also been reported by others in similar studies (18).

The amount of leaching time which varied from 6 to 24 hours, did not affect the agreement between the two procedures, suggesting that with the degree of acidification used, the dissolution of any absorbed trace metals occurred within 6 hours. However, for consistency, a 24 hour leaching period in the sample container after post-acidification was adopted. Thus, with the problems encountered with pre-acidification, such as (1) the inability to gauge precipitation amount a priori, (2) the evaporation of the acid spike prior to the event, and (3) potential for contamination due to the exposure of sampling equipment to the concentrated acid pre-spike, post-acidification is the preferred method.

Biological activity can alter the chemical makeup of precipitation samples in storage (16). It was assumed that acidification of the samples to less than pH2 by the addition of 0.2% v/v Q-HCl would inhibit biological growth. However, after several months of storage in the dark, at room temperature, some

precipitation samples developed a black fungus-like growth which increased in size with time. After this discovery, the acid spike was then doubled to 0.4 v/v Q-HCl and no biological growth was detected after many months of storage.

Sample Storage

Samples are returned from the field, removed from the transport bags, weighed to determine volume and acidified to below pH1.6 (0.4% v/v Q-HCl) directly in the sample containers by the addition of quartz distilled acid spikes. The samples are then securely covered with a plastic bag, and placed in a clean bench. Approximately twenty-four hours later, the samples are homogenized by swirling the containers, and 20 to 30 mls used to repeatedly rinse the pre-cleaned storage bottles of sufficient volume to hold the entire sample. After rinsing, the remaining volume is transferred to the storage bottle which is securely capped and placed in appropriate size plastic bags, sealed and stored until subsequent analysis. Samples stored in this manner are stable for at least 1 year.

Operational Blanks

The amount of contamination from the material and methods used in the collection and analysis of trace metal precipitation samples is monitored routinely by operational field blanks. These blank experiments are conducted on a bi-monthly basis or when 1) a change in field operator occurs, 2) a new batch of spike acid, liner bags, or storage bottles are used, or 3) any changes occur near the sample site, such as any equipment changes at the site or or unusual activity in the surroundings (e.g. construction, excavation, traffic). The blanks consist of substituting MQ-water for the samples as follows: in the field 200-1000 mls of MQ-water is added to the ACM or manual bulk collector installed as previously discussed. A 50 ml portion of the MQ-water is saved and labeled

as "process blank". Field blanks are conducted with the collectors in the closed position (either by unplugging the power to the ACM or covering the MB with a plastic bag). Approximately twenty-four hours later, the blank solutions are retrieved, appropriately labelled, and processed in the same manner as precipitation samples.

Analysis

To minimize contamination, all sample manipulation is carried out in a laminar flow clean-bench using scrupulously acid-cleaned materials. To monitor for any contamination during preparation and analysis, analytical blanks of Q-water are processed in the same manner as samples. The concentration of Cd, Cu, Fe, Mn, Pb, and Zn in precipitation are determined directly by graphite furnace atomic absorption spectroscopy (GFAA). An Instrumentation Laboratory Model 951 atomic absorption spectrophotometer is used together with a Model 555 graphite furnace and Model 254 Fastac auto sampler. Primary standards consisted of Spex hi-purity metals (Spex Industries, Inc. Edison, New Jersey) dissolved in 2% Q-HCl. Calibration was made against secondary metal standards diluted into a acid solution of 0.4% v/v Q-HCl to duplicate the sample matrix. Nickel and vanadium concentrations in precipitation are determined by GFAA after 5-20 fold concentration by evaporation under a clean-bench in teflon beakers, and subsequently redissolved in 0.1% Q-HNO₃. Separate Ni and V standards are made in 0.1% Q-HNO₃. The instrument settings used for the determination of the measured metals by furnace AA are given in Table III.

To determine the accuracy of these methods, several quasi-independent techniques are employed using sub-aliquots from samples representing the range of sample matrices.

1. Direct analysis by GFAA with standard calibration curves.

TABLE III

Instrumental parameters for Instrumentation Laboratory Model 951 Atomic Absorption Spectrophotometer equipped with Model 254 Fastac auto-sampler and 555 atomizer for the determination of trace metals in wet deposition.

<u>Metals</u>	<u>254 Deposition sec</u>	<u>Char.1 °C/sec</u>	<u>Char.2 °C/sec</u>	<u>Atomize 1 °C/sec</u>	<u>Atomize 2 °C/sec</u>	<u>Comments</u>
Fe, Zn	5 ¹ , 10 ²	600/25	650/5	2400/0	2400/10	
Cu, Mn	5 ¹ , 20 ²	950/25	1000/5	2250/0	2250/10	
Pb, Cd	10 ¹ , 25 ²	400/20	450/5	1700/0	2250/5	Microboat
Ni	20 ¹ , 40 ²	700/20	700/5	2350/0	2350/5	
V	30 ¹ , 50 ²	500/15	750/15	2500/0	2500/10	

¹Lewes samples

²Bermuda samples

2. Direct analysis by GFAA with standard addition.
3. Pre-concentration by APDC/DDDC/freon extraction into 0.1N Q-HNO₃ prior to GFAA (23).

RESULTS AND DISCUSSION

Analysis

Interferences

Major ions in sufficient concentration can interfere with the direct determination of trace metals in GFAA in aqueous solutions. Minute concentrations of sea salt in precipitation have been shown to suppress Cd, Pb, and Zn signal resulting in errors of up to 25% when concentrations are calculated from standard curves of dilute acid standards (18). The major ion composition of wet deposition sampled at the mid-Atlantic coast and the western Atlantic were reported in concentrations much less than seawater, but higher than is common at inland sites (24). Comparison of the results obtained from selected precipitation samples in which a portion was directly analyzed with standard curve calibration and the remainder analyzed after separation by extraction from the major ion matrix indicates that with the proper pyrolysis program and background corrections (reported in Table III), the major ion matrix is not a problem in the direct analysis of Cd, Cu, Fe, Mn and Zn. However, the Pb signal is significantly suppressed. The substitution of a rectangular GFAA cuvette with microboat eliminates salt suppression of Pb and the need for standard additions or extraction. The presence of the microboat platform delays atomization until the atmosphere in the furnace is at a higher and more constant temperature, reducing vapor-phase interferences and matrix effects caused by salts (25).

Precision and Accuracy

The overall analytical precision of trace metal determinations in precipitation is estimated from the average of the standard deviations calculated from all the samples analyzed. Usually, duplicate determination of two to three separate aliquots of each sample is involved depending upon volume. Thus, this estimates both the reproducibility of the GFAA technique and the associated problems of maintaining homogeneity of sub samples. For all of the metals, the average overall precision averages about 10% of the average metal concentration reported for the two locations (Table IV).

The accuracy of the analysis is maintained by frequent calibration against dilute high purity metal standards. The calibration of the GFAA technique was checked by several quasi-independent techniques including standard curve calibration, standard additions and separation/preconcentration of the metals prior to analysis. Results obtained by the various techniques were within 10% for all the metals investigated. The exception is Pb, which as described earlier, is subjected to salt suppression, requiring the use of a modified GFAA cuvette.

Blanks

Operational field and process blanks are tested throughout the sampling period. The process blank is a measure of the metal contribution derived from the storage bottles, reagents and analytical procedures. The average concentration of the process blanks, in $\mu\text{g/l}$, are: $\text{Cd} < 0.005$, $\text{Cu} < 0.02$, $\text{Fe} < 0.01$, $\text{Mn} < 0.005$, $\text{Ni} < 0.01$, $\text{Pb} < 0.01$, $\text{V} < 0.001$, $\text{Zn} < 0.01$, which are negligible when compared to the average precipitation concentrations. The field blanks estimate contamination from the collector materials and during the field and laboratory operations, including transport, deployment, recovery, sample acidification and partitioning. The

TABLE IV

The overall average precision of trace metal concentration ($\mu\text{g/l}$) in precipitation at Lewes, Delaware and High Point, Bermuda as determined by replicate analysis of all samples from the summer of 1982 through December 1983 and as percent of the monthly average concentration.

Metal	High Point, Bermuda			Lewes, Delaware		
	Precision	Conc. $\mu\text{g/l}$	Percent	Precision	Conc. $\mu\text{g/l}$	Percent
		Avg. Mo. Conc. ¹			Avg. Mo. Conc. ¹	
Cd	0.008	0.062	13	0.03	0.18	17
Cu	0.03	0.32	9	0.12	0.68	18
Fe	0.41	2.94	14	1.23	15.4	8
Mn	0.030	0.218	14	0.15	1.36	11
Ni	0.019	0.167	11	0.03	0.79	4
Pb	0.070	0.722	10	0.35	3.02	12
V	0.013	0.096	14	0.04	0.67	6
Zn	0.20	1.53	13	0.38	6.38	6

¹From Church, et.al. (20).

TABLE V

Average operational field blanks for trace metal determination in precipitation at Lewes, Delaware and High Point, Bermuda as a percent of the monthly average concentration ($\mu\text{g/l}$).

Metal	High Point, Bermuda			Lewes, Delaware		
	Field Blank	Avg. Mo. Conc. $\mu\text{g/l}$ Conc. ¹	Percent	Field Blank	Avg. Mo. Conc. $\mu\text{g/l}$ Conc. ¹	Percent
Cd	0.006	0.062	9.7	0.01	0.18	5.6
Cu	0.03	0.32	9.4	0.06	0.68	8.8
Fe	0.09	2.94	3.1	0.38	15.4	2.5
Mn	0.017	0.218	7.8	0.05	1.36	3.7
Ni	0.010	0.167	6.0	0.04	0.79	5.1
Pb	0.022	0.722	3.0	0.13	3.02	4.3
V	0.004	0.096	4.2	0.01	0.67	1.5
Zn	0.06	1.53	3.9	0.19	6.38	3.0

¹From Church, et.al. (20).

average levels for the field blank in $\mu\text{g}/\text{l}$ and as a percentage of the monthly average concentration in wet deposition are reported for the two sample sites in (Table V).

The operational blanks at both sampling locations are only on the order of 2 to 10 percent of the average metal content of precipitation at the coastal and open western Atlantic as reported by Church, et.al. (20). The blanks concentration are somewhat higher in Lewes than Bermuda probably due to the comparatively high ambient aerosol trace metal burden in the continental environment (G. Wolff, personal communication).

Particulate trace metals in wet deposition

Some particulate material from local and remote sources are, by way of washout, included in wet deposition samples. In order to determine the total wet flux from precipitation samples, it is necessary to analyze both the dissolved and particulate trace metals. Thus, any particulate trace metals must be either converted to, or analyzed along with, the dissolved material. The amount of particulate Zn, Cd, Pb and Cu in precipitation samples of ambient acidity have been shown to be small ($<10\%$) (17,26) and should be reduced even further by acidification of the samples. In order to determine the amount of particulate trace metals in samples acidified as specified by the protocol in this study, the following experiment was conducted. To maximize the potential particulate load, six small event (0.24-1.33 cm) samples collected at Lewes, Delaware after dry periods of 5 to 12 days during the spring to early fall were selected. Samples have been post-acidified to $\text{pH} \sim 2$ according to the sampling protocol. Aliquots of each sample were centrifuged at 1300 G's for 30 minutes and analyzed side-by-side with non-centrifuged portions. A comparison of the concentrations from the two treatments indicate insignificant ($<10\%$) particulate forms of Cd, Cu, Ni, Pb and Zn present. However, centrifugation removed an average of 17% of the Fe and 21% of the

Mn from these precipitation samples. Both Fe and Mn have large crustal sources which may explain the presence of these refractory particulate forms.

The presence of significant particulate Fe and Mn in acidified precipitation samples necessitates maintaining sample homogeneity, so that both dissolved and particulate trace metals are introduced into the graphite furnace, in the same proportions as in the original sample, and analyzed in total. Thus, samples are thoroughly shaken during all partitioning steps and analyzed within a few hours after their placement into the IL 254 auto-sampler changer.

A second experiment was conducted to further test if total metal concentrations are determined and to estimate sample storage stability. Nine samples were analyzed for Fe at storage intervals ranging from a few days to 1 year. Results of this experiment revealed that Fe concentration did not significantly change ($\leq 5\%$) over the time period tested. Since long term storage under acid conditions would most likely change the dissolved-particulate distribution, these results indicate that the total concentration is determined and the samples are well preserved and accurately analyzed in total. Thus, we are confident that the concentrations of trace metals in precipitation measured by our method are representative of total wet deposition (dissolved plus particulate).

Sampling Accuracy

The accuracy of our automated sampling protocols was checked by simultaneously deploying manual bulk (MB) collectors and comparing the results. The MB collector was selected because of its simple and convenient all-plastic construction, and because of its widespread use by other investigators (2,6,19). Also, in this study, the higher deployment elevation of the MB collector (3 vs. 1 m for the ACM) should render it less susceptible to

ground-based contamination. Comparisons between the two collectors were made on more than 25 occasions at both sampling sites over the course of study. Twenty-six percent of the comparisons made at Lewes and thirty-six percent at Bermuda were rejected because the manual collector was not opened at the onset of the precipitation event or one or both of the collectors was visibly compromised with local debris. The average weighted concentration calculated from the ACM and MB collectors for the remaining events agree to within 20% for all metals except Cu (31%) at Lewes (Table VI). This is excellent agreement considering 1) the large natural spatial variability of trace metals in precipitation (18,26) which would occur independent of any sampling artifacts, and 2) the different geometry and sampling efficiency of the two systems. The only consistent trend which appeared at both locations was that on the average MB collected more Fe relative to the ACM. This trend might be expected due to the manual operation of the MB which results in longer exposure time to the atmosphere resulting in the inclusion of more particulate material when precipitation was not occurring. Thus the ACM results may be a more accurate estimate of Fe concentration in wet deposition. Overall, we feel our results are accurate and that trace metals in precipitation, can be successfully collected using appropriately modified automatic collectors.

Conclusion

This paper presents a method for accurately collecting and analyzing trace metals in precipitation in semi-remote coastal and open oceanic areas of the western Atlantic. The procedure has been used successfully at Lewes, Delaware and on Bermuda over a three year period as part of the WATOX program. The procedure uses a modified automatic collector, with a gusseted polyethylene bag to line the collector bucket, to sample wet deposition events, the accuracy of which is randomly checked by simultaneously deploying a manually operated coupled funnel-bottle collector.

TABLE VI

A comparison of the volume-weighted mean concentration ($\mu\text{g}/\text{l}$) measured by simultaneously deployed automatic (ACM) and manual (MB) samplers at Lewes, Delaware and High Point, Bermuda.

<u>Collector</u>	<u>Concentration ($\mu\text{g}/\text{l}$)</u>					
	<u>Cd</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Pb</u>	<u>Zn</u>
Lewes, Delaware						
ACM	0.172	1.18	16.4	1.40	3.17	5.39
MB	0.133	0.81	18.2	1.62	2.80	4.69
High Point, Bermuda						
ACM	0.041	0.223	6.21	1.10	0.48	1.30
MB	0.043	0.261	7.56	1.08	0.50	1.62

All collector vessels must be rigorously acid cleaned prior to use. Post-acidification of the sample and 24 hour leaching by the addition of 0.4% (v/v) ultra pure hydrochloric acid after the event sample acidification is necessary to assure quantitative recovery and preserve the sample. A filtered air environment (clean hood or bench) is recommended for preventing contamination during plastic ware cleaning, sample acidification, and transfer to storage bottles. Sample analysis is preformed by atomic absorption spectrophotometry with heated graphite atomization directly or by evaporative pre-concentration. Sample homogeneity must be maintained during all sample partitioning steps and analysis. Identical field and process blanks must be run to assure accurate results and identify contaminated samples. At each site, protocols for siting and acceptability of automated collection must be verified by parallel manual collections and field blanks.

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REFERENCES

1. Windom, H. L. 1981. In: River inputs to ocean systems. UNEP and UNESCO, 360-369.
2. Jickells, T., A. H. Knap and T. M. Church. 1984. J. Geophys. Res. 89:1423-1428.
3. Buat-Menard, P., U. Ezat, and A. Gaudichet. 1983. In: Precipitation Scavenging, Dry Deposition, and Resuspension. [eds]. Elsevier.
4. Jickells, T., A. Knap and W. Deuser. 1985. Deep-Sea Res. 31:1169.
5. Bertine, K. K. and E. D. Goldberg. 1971. Science 173:233-235.
6. Galloway, J. N., G. E. Likens, W. Keene and J. M. Miller. 1982a. J. Geophys. Res. 87:8771-8786.
7. Goodman, G. T. and T. M. Roberts. 1971. Nature 231:287-292.
8. Klein, D. H. 1972. Env. Sci. and Tech. 6:560-562.
9. Livett, E. A., T. A. Lee and J. H. Tallis. 1979. J. Ecology 67:865-891.
10. Norton, S. A., D. W. Hanson and R. J. Campana. 1980. In: Effects of air pollutants on Mediterranean and temperate forest ecosystems. Miller (ed.).
11. Settle, D. M. and C. C. Patterson. 1982. J. Geophys. Res., 87:8857-8869.
12. Lantzy, R. J. and F. T. Mackenzie. 1979. Geochim. Cosmochim. Acta 43:511-525.
13. Galloway, J. N., J. D. Thornton, S. A. Norton, H. L. Volchok and R.A.N. McLean. 1982b. Atm. Env. 16:1677-1700.
14. Johnson, A. H. and T. J. Siccamo. 1983. Env. Sci. Tech. 17:294A-305A.
15. Graedel, T. E. and C. J. Weschler. 1981. Reviews of Geophys. and Space Phys. 19:505-539.
16. Galloway, J. N., C. Hall and G. E. Likens. 1977. Tellus 30:71-82.

17. Nurnberg, H. W., P. Valenta, V. D. Nguyen, M. Godde, and E. Urano de Carvalho. 1984. *Fresenius J. Anal. Chem.* 317:314-323.
18. Haraldsson, C. and B. Magnusson. 1983. *Proceedings: International Conference on Heavy Metals in the Environment, Heidelberg* 1:82-86.
19. Arimoto, R., R. A. Duce, B. J. Ray and C. K. Unni. 1985. *J. Geophys. Res.* 90:2391-2408.
20. Church, T. M., J. M. Tramontano, J. R. Scudlark, T. D. Jickells, J. J. Tokos and A. H. Knap. 1984. *Atm. Env.* 18:2657-2664.
21. WMO. 1974. *WMO operation manual for sampling and analysis techniques for chemical constituents in air and precipitation.* WMO Publ. No. 299, Geneva, Switzerland.
22. Galloway, J. N. and G. E. Likens. 1976. *Water Air Soil Pollut.* 6:241-258.
23. Danielsson, L. G., B. Magnusson and S. Westerlund. 1978. *Analytical Chimica Acta* 98:47-57.
24. Church, T. M., J. N. Galloway, T. D. Jickells and A. H. Knap. 1982. *J. Geophys. Res.* 87:11013-11018.
25. Conley, M. K., J. S. Sortera and H. L. Kahn. 1981. *Instrumentation Laboratory Report No. 149.* 7 pp.
26. Lindberg, S. E. and R. R. Turner. 1983. *Proceedings: International Conference on Heavy Metals in the Environment, Heidelberg*, 1:107-114.

MONITORING TRACE METALS IN PRECIPITATION: THE ONTARIO EXPERIENCE

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INTRODUCTION

The Ontario Ministry of the Environment has been active in the measurement of trace metals in precipitation since the 1970's. The initial effort was in the form of funding university research projects in Northern Ontario (Kramer, 1973, 1975 and 1976). Later on, as part of the Sudbury Environmental Study (SES) in understanding the emissions and their fate in the atmosphere of the Sudbury smelter sources, precipitation network constituted an integral part of the study (Chan and Lusi, 1985). In 1979, a major multidisciplinary study, Acidic Precipitation in Ontario Study (APIOS), was launched to study the long-range transport of air pollutants and the acid rain phenomenon. Monitoring of trace metals in precipitation was expanded from a local to a regional scale, covering the whole province of Ontario (Chan et al., 1985 a,b).

In this account, discussion will be focussed on Ontario's experience in sampling of trace metals in precipitation associated with SES and APIOS.

SAMPLING PROGRAM

There are three areas which are of primary concern in the operation of a monitoring network, i.e. sampler, sampling frequency and sampled parameters. Quality assurance is necessary to ensure that data produced are complete, representative, precise and accurate. The choice of sampler should ensure sample integrity and is often dictated by financial constraints. Both sampling frequency and sampled parameters reflect the objectives of the network. Sampling techniques and quality assurance for measurements of wet deposition have been discussed by Vet (1983) and Chan (1983) respectively.

Sampler and Sampling Interval

From our experience, for long term wet deposition pattern evaluation, it is adequate to sample with a wet-only sampler over a monthly period. However, for source receptor relationship studies, a higher time resolution of no longer than 24 hours is necessary. Significant advances have been made on precipitation chemistry sampling instrumentation. Many of the earlier studies employed bulk samplers over prolonged sampling periods. Nowadays, moisture activated wet-only samplers are commercially available.

In both SES and APIOS, long term wet deposition pattern of trace metals is determined using Sangamo (MIC) wet-only samplers over a period of up to one month. In the former case, precipitation samples were collected directly into the black polyethylene buckets. In the latter case, a polyethylene/nylon laminated bag inserted into the bucket serves as the collection vessel for precipitation samples.

In the assessment of the relative importance of wet deposition of the Sudbury source emissions to the local background contribution, daily sampling was carried out using a large open mouth bucket with a polyethylene bag insert. With very careful choice of sampling sites, it is felt that sampling over a 24 hour period with a bulk sampler would yield comparable results to those of a wet-only sampler.

Due to the fact that precipitation samplers have less than perfect collection efficiency, precipitation depth which is needed for deposition calculations is determined from either a standard rain gauge or a Nipher-shielded snow gauge.

Chemical Parameters and Sorption on Surfaces

The trace metals selected for study are similar in both SES and APIOS. The choices reflect their emission rates from the studied sources and the effects associated with their deposition on ecosystems.

Adsorption of trace metals in water samples on polythene surfaces have long been recognized. The extent of the problem varies from one metal to

another and is a function of sample acidity.

In order to produce chemical results representative of the original incident precipitation, investigations were carried out into the sorption properties (absorption and desorption) of selected metals on Sangamo bucket and polyethylene bag surfaces as well as procedures to determine the adsorbed amounts on the surfaces.

Our laboratory study (Chan et al., 1983) indicated that desorption of trace metals (Fe, Cu, Ni, Pb, Mn and Zn) was not detectable when bags were leached with distilled water and 5% HNO_3 . Adsorption of trace metals (Fe, Cu, Ni, Pb, Cd and Cr) with concentrations up to 50 ug l^{-1} on polyethylene bags over 24 hours was also negligible. Loss of Zn and Al on polyethylene surfaces could be as high as 20% over 1 day.

The situation is rather different when the residence time of the samples in the container is extended to over a month. At pH (4.1 to 4.4) representative of typical precipitation pH of N. American samples, adsorption of Ni, Pb and Mn was found to be minimal over 29 days and that of Cd was about 10%. Fe, Cu, Zn and Al had adsorption losses ranging from 26% to 47% over the same interval. Leaching with 5% HNO_3 was found to be effective to desorb the lost metals from the surfaces.

The sorption properties of trace metals have been further evaluated using field samples. By comparing the leachate from the bag using 5% HNO_3 to the sum of the amounts in the leachate and free solution, adsorption losses of trace metals were determined. Based on about 1,700 samples, the median adsorption loss values were 38.5%, 37.4%, 15.5% and 26.6% respectively for Fe, Cu, Zn and Al, and are consistent with the laboratory results. However, contrary to what the initial laboratory study did not indicate, based on about 1200 samples, Pb adsorption loss on polyethylene loss was found to be 19.5%.

Sampling Protocol, Chemical Analysis and Quality Assurance Program

Details of the sampling equipment, procedures, sample handling have been documented elsewhere (Chan et al., 1985b). Chemical analyses of the

trace metals studied are carried out by the Ministry's Laboratory Services Branch in Toronto by either flameless atomic absorption spectroscopy (Ni, Pb, Cd and V) or inductively coupled plasma (Zn, Fe Al, Mn and V). Details will be presented by Loescher (1986) in this workshop.

In order to produce representative, high quality data, a quality assurance program covering all components, namely field, laboratory and data management in the APIOS deposition monitoring program has been implemented. Details are given elsewhere (Bardswick, 1983 and MOE, 1985).

Precision expressed in terms of sampling reproducibility $(1 - |\Delta C| / C)$ where ΔC is the difference of duplicate measurements and C corresponds to either one of the duplicate measurements) is typically better than 75% for Mn, Zn, Fe, Pb, Al and Cu precipitation concentration measurements over a 28 d period using a Sangamo (MIC) sampler (Chan et al., 1986a).

There is no simple way to assess the accuracy of precipitation chemistry measurements. It can be approximated by subjecting standard solutions or composites of precipitation samples of known chemical concentrations to steps of the sampling scheme. Accuracy can be investigated in terms of evaporative losses and dry deposition being a source of error. The assessment on trace metal concentration measurements over a 28d period has not yet been completed. However, based on the assessment of acid/base-related parameters, on average, less than 10% evaporative losses were found. Dry deposition is observable for soil-related parameters, and could be as high as 10 to 30% (Chan et al., 1986a). Therefore, it is not unreasonable to speculate that the measurement accuracy of trace metals is no better than that of acid/base parameters, namely less than 90%.

RESULTS

Quality results of trace metals in precipitation are sparse and are necessary in the assessment of the role played by trace metals in the environment.

In Ontario, precipitation trace metal chemistry data have been used to evaluate precipitation quality and wet deposition (Chan et al., 1986b), the fate of point source emissions and the relative importance of point source vs. background contributions (Chan and Lysis, 1985), the relative importance of wet to dry deposition and scavenging ratios (Chan et al., 1986b). Details of the results have been presented elsewhere and therefore will not be repeated here.

REFERENCES

Bardswick, W.S. (1983), Acidic Precipitation in Ontario Study -Technical and Operating Manual.

Chan, W.H. (1983), "Quality Assurance - Monitoring of Wet Deposition", Proceedings of Symposium on Monitoring and Assessment of Airborne Pollutants with Special Emphasis on Long-Range Transport and Deposition of Acidic Materials, Eds, Pierce, R.C., Whelpdale, D.M. and Sheffer, M.G. NRCC 20642.

Chan, W.H., Tomassini, F. and Loescher, B. (1983), Atmos. Environ. 17, 1779-1785.

Chan, W.H. and Lysis, M.A. (1985), Water, Air and Soil Pollution, 26, 43-58.

Chan, W.H., Orr, D.B., Bardswick, W.S. and Vet, R.J. (1985a), Acidic Precipitation in Ontario Study - An Overview. The Event Wet/Dry Deposition Network (1st revised edition), Ontario Ministry of the Environment Report ARB-142-85-AQM.

Chan, W.H., Orr, D.B., Bardswick, W.S. and Vet, R.J. (1985b), Acidic Precipitation in Ontario Study - An Overview. The Cumulative Wet/Dry Deposition Network (2nd revised edition), Ontario Ministry of the Environment Report ARB-141-85-AQM.

Chan, W.H., Tang, A.J.S., Orr, D.B., Bardswick, W.S. and Lysis, M.A. (1986a) "An Evaluation of Sampler Types and Sampling Periods for Measurements of Wet and Dry Deposition", Ontario Ministry of the Environment Report ARB-98-85-

AQM, to be published.

Chan, W.H., Tang, A.J.S., Chung, D.H.S. and Lusi, M.A. (1986b), to appear in Water, Air and Soil Pollution.

Kramer, J.R. (1973, 1975, 1976), Fate of Atmospheric Sulphur Dioxide and Related Substance as Indicated by Chemistry of Precipitation", McMaster University, Dept. of Geology Reports.

Loescher, B. (1986), Presented at this workshop.

MOE (1985), Acidic Precipitation in Ontario Study - Quality Assurance Manual, Ontario Ministry of the Environment Report ARB-051-85-AQM.

Vet, R.J. (1983), "A review of Current Wet Deposition Measurement Techniques", Proceedings of Symposium on Monitoring and Assessment of Airborne Pollutants with Special Emphasis on Long-Range Transport and Deposition of Acidic Materials, Eds, Pierce, R.C., Whelpdale, D.M. and Sheffer, M.G. NRCC 20642.

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APPLICATION OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS
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INTRODUCTION

The analysis of wet atmospheric deposition as it relates to acid precipitation studies has come under intense scrutiny by many laboratories throughout the industrialized world. In particular the determination of co-contaminants of acid precipitation (rain and snow) has been investigated using a variety of techniques and methods. Although the analysis of major ions (e.g. sulphates, nitrates, chlorides, magnesium, sodium and potassium) are relatively easy to undertake, the case for metals and halides (other than chlorine) can be significantly more complex. By far the most widely used technique for metal analysis in rain or snow is graphite furnace atomic absorption spectrophotometry. However, this method is not used for more than a handful of trace elements and can be severely compromised by matrix effects.

Other methods have included flame photometry, colorimetry, nephelometry and UV spectrophotometry. In the recent past inductively coupled plasma-atomic emission spectroscopy (ICP-AES) has shown good success in determining many elements simultaneously, in particular total sulphur (Landsberger et al., 1985a).

The use of nuclear methods in environmental analytical chemistry has received a great deal of attention in the last decade. Techniques such as instrumental neutron activation analysis (NAA), photon activation analysis, x-ray fluorescence, and the more recent proton-induced x-ray emission have all been successfully employed in various environmental, biological and toxicological studies. With respect to air pollution investigations NAA has been extensively utilized in many urban, rural and remote aerosol studies and numerous papers have been reported.

Surprisingly the sensitive methods of NAA have not often been fully exploited for rain and snow investigations. During the 1970's several investigators began using NAA techniques to determine a plethora of elements in rainwater, snow and ice cores. Rancitelli and Perkins (1970) analysed rain for nineteen elements using a very high thermal flux. One of the first systematic studies of precipitation chemistry was done by Cawse and Peirson (1972) and Peirson et al. (1973). Twenty-seven trace elements were detected in rainwater in the rural site of Wraymires, England. The use of washout factor and dry deposition velocity rates permitted the identification of trace elements coming from soil-derived, maritime or industrial environments. Subsequent investigations have been reported later by Cawse (1975-1978, 1980-1981). Tanner et al. (1972) used elaborate chemical separation methods to determine upwards to nineteen elements in rainwater and ice cores from Greenland. Bogen (1973) measured concentrations of many elements in cloud and rain water. Salmon (1975) wrote an excellent report on the use of NAA in environmental studies, including wet atmospheric deposition. Possible marine, crustal and industrial sources of several trace elements along with their respective nuclear properties and interfering nuclides, were described. Luten (1976) and Merritt (1976) have also reported other findings using NAA techniques. Barrie (1980) and Barrie and Walmsley (1978) employed NAA in conjunction with other techniques and determined ambient concentrations, deposition patterns and deposition rates of several elements in air and snow around a thermal generating station. Other works have included the effect of seasonal cycling of trace elements in rainfall (Beavington and Cawse, 1979) and the experimental problems and interpretation of rainfall results (Slanina et al. 1979a,b). Both Schuyster et al. (1978) and Hamilton and Chatt (1982) provided a systematic method for the detection of insoluble and soluble fractions of atmospheric wet deposition. Landsberger et al.

(1983) gave an in depth analysis of urban snow using NAA along with proton-induced x-ray emission techniques. Recently Drake et al. (1986) have successfully employed NAA to routinely determine ten trace elements in urban rainfall as part of a comprehensive rain network system. Other uses for NAA have included the analysis of snow from the Antarctic regions (Boutron 1979a,b).

It is the intention of this paper to re-assess the use of NAA in wet atmospheric deposition studies in routine environmental analysis. Emphasis is placed on optimization of the various NAA methods which can be used as well as the use of certified reference materials to ensure quality control. The reader is referred to review articles discussing the application of nuclear methods in trace analysis of wet atmospheric deposition (Landsberger et al., 1985b) and the environmental importance of studying these various trace constituents (Galloway et al., 1982 and Campbell et al., 1985).

SAMPLE PREPARATION AND METHOD OF ANALYSIS

Analysis of the usually low elemental abundances found in wet atmospheric deposition prescribes very careful handling of the samples both in the field and laboratory environments. Contamination from many sources can seriously jeopardize the final results. Rain and snow samples can be prepared in various fashions and have been outlined by Landsberger et al. (1985b). Suffice to state that the ideal situation for analysis is to preclude any sort of preconcentration methods as to minimize contamination.

The properties of the nuclear reactions producing short-, medium- and long-lived nuclides are shown in tables 1 and 2. Upwards to

TABLE 1

Properties of Reactions Producing Short-Lived Nuclides

Element	Reaction (n, γ)	<u>Radionuclide properties</u>	
		Half-life	Gamma energies used (keV)
Ag	^{110}Ag	24.3 sec	657.8
Al	^{28}Al	2.24 min	1778.9
Ba	^{139}Ba	83.2 min	165.9
Br	^{80}Br	17.4 min	617.0
Ca	^{49}Ca	8.7 min	3084.4
Cl	^{38}Cl	37.3 min	1642.0, 2167.8
Co	$^{60\text{m}}\text{Co}$	10.48 min	58.6
Cu	^{66}Cu	5.1 min	1039.0
Dy	^{165}Dy	2.33 hr	94.7
F	^{20}F	11.0 sec	1633.8
I	^{128}I	25.0 min	442.3
In	$^{116\text{m}}\text{In}$	52.4 min	416.9, 1097.3, 1293.5
K	^{42}K	12.36 hr	1524.7
Mg	^{27}Mg	9.5 min	843.8, 1014.4
Mn	^{56}Mn	2.58 hr	846.7, 1810.7
Na	^{24}Na	15.0 hr	1368.4, 2754.1
Se	$^{77\text{m}}\text{Se}$	17.4 sec	161.7
Sr	$^{87\text{m}}\text{Sr}$	2.81 hr	388.4
Ti	^{51}Ti	5.8 min	320.1
U	^{239}U	23.5 min	74.6
V	^{52}V	3.8 min	1434.2

TABLE 2
Properties of Reactions Producing Medium-and
Long-Lived Nuclides

Element	Reaction (n, γ)	Half-life	<u>Radionuclide properties</u>
			Gamma energies used (keV)
As	^{76}As	26.3 hr	559.1
Au	^{198}Au	2.7 d	411.8
Br	^{82}Br	35.3 hr	554.3, 776.5
Ga	^{72}Ga	14.1 hr	834.0, 629.9
K	^{42}K	12.36 hr	1524.7
La	^{140}La	40.23 hr	1596.2
Lu	^{177}Lu	6.71 d	208.4
Mo	^{99}Mo	66.02 hr	140.5
Na	^{24}Na	15.0 hr	1368.4, 2754.1
Sb	^{122}Sb	2.72 d	564.0
Sm	^{153}Sm	47.0 hr	103.2
W	^{187}W	23.9 hr	685.8
Long-lived			
Ag	$^{110\text{m}}\text{Ag}$	252 d	658.8
Ce	^{141}Ce	32.5 d	145.4
Cr	^{51}Cr	27.72 d	320.0
Cs	^{134}Cs	2.06 yr	795.6
Co	^{60}Co	5.27 yr	1173.2, 1332.4
Eu	^{152}Eu	13.0 yr	1408.0
Fe	^{59}Fe	45 d	1098.2, 1291.6
Hg	^{203}Hg	46.60 d	279.2
Rb	^{86}Rb	18.7 d	1076.6
Sb	^{124}Sb	60.2 d	602.7
Sc	^{46}Sc	83.8 d	889.3
Se	^{75}Se	118.5 d	136.0, 264.7
Th	^{233}Pa	27.0 d	311.9
Zn	^{65}Zn	243.8 d	1115.5

forty-five elements (and several more) can be determined with good precision and accuracy. However quite often preconcentration methods, preferably freeze-drying ones, are usually needed for the analysis of the longer-lived nuclides (see table 2).

As part of extensive research and contract programs funded by Atmospheric Environment Service (AES Environment Canada) and the Ontario Ministry of the Environment (OME) to the McMaster Nuclear Reactor, Nuclear Activation Services Limited (located in the nuclear reactor), and the Department of Geography, methods have been developed in INAA specifically to analyze rain and aerosol samples from the Dorset (OME), Alert, Arctic (AES) and Hamilton (Dept. of Geography) environmental stations. Only the results for the rain samples from Dorset will be discussed here. This station can be considered to represent a rural/remote region.

All samples and blanks were supplied by AES or OME. The first goal was to ascertain which elements could be determined without any preconcentration procedures. Upwards to ten elements (Al, Br, Ca, Cl, Cu, I, Mg, Mn, Na and V) could be readily analysed with good sensitivities (see table 3). Potassium had a high detection limit and was usually determined with longer irradiation times. Of particular importance is that NAA is very well suited to determine three halogens (Br, Cl and I). The importance of bromine in Pb/Br ratios is very well known and iodine and chlorine give important insight into marine source influences. Typically for a 4-5 mL sample an irradiation time of ten minutes, a delay time 1-2 minutes and a counting time of ten minutes were employed. The use of an adequate neutron flux (in our case $5 \times 10^{12} \text{ n.cm}^{-2}/\text{sec}$) and a high efficiency germanium counter (greater than 20%) ensured good sensitivities for the above

TABLE 3

Typical Detection Limits for Dorset
Rainwater Samples (Unconcentrated)

<u>Element</u>	<u>Detection Limit</u> (ng/g)
Al	0.6
Br	1
Ca	27
Cl	8
Cu	5
I	0.8
K	300
Mg	90
Mn	0.3
Na	9
V	0.05

elements. The analysis of the medium- and long-lived nuclides almost always needs the use of some sort of preconcentration method. Several are available but the method of choice is usually freeze-drying. Several authors have shown the reliability of such techniques (Landsberger et al 1983). The most important aspects to consider are the preconcentration factor (which should be at least one hundred fold) (see table 4) and the irradiation time in the reactor. Several hours is usually a suitable length of time (providing that a good preconcentration factor is obtained). Radiolysis is a common phenomena and quite often the samples may leak or even explode. One way to overcome this problem is to enclose the sample in a quartz vial. However this will increase the cost quite substantially and may not be suitable for a long term routine environmental program. Another solution is to freeze-dry the complete filtrate in a polyethylene bag and subsequently irradiate the sealed bag. However this procedure may lead to some serious contamination from the bags themselves.

The determination of the particulate matter of filtered rain and snow has not received nearly as much attention as bulk analysis. In fact a perusal of the literature reveals that many studies do not employ filtration methods and meaningful environmental comparisons (with those studies that do) are hard to achieve and can often lead to misleading results. Unfortunately no clear and unambiguous methods have been adopted by the environmental community. A simple but effective methodology is given by Landsberger et. al (1983).

Detection limits for the Dorset particulate matter can vary depending on the amount of rain filtered. In our present investigation between 180 mL - 1200 mL were filtered for sampling events. Results for an average 500 mL of filtered rainwater is shown in Table 5. Several filters were analysed for blank contamination. The

TABLE 4

Typical Detection Limits for Dorset

Rainwater Samples (Concentrated)

<u>Element</u>	<u>Detection Limit</u> (ng/g)
As	0.07
Ce	3
Cr	4
Co	0.5
Eu	0.3
Fe	400
K	20
La	0.04
Sb	0.06
Sc	0.04
Sm	0.01
Zn	15

TABLE 5

Typical Detection Limits for Dorset

Rain Particulate Matter (500 ml)

<u>Element</u>	<u>Detection Limit</u> (ng)
Ag	10
Al	60
As	1
Ba	500
Br	40
Ca	600
Ce	20
Cl	600
Co	3
Cr	20
Cu	170
Eu	0.8
Fe	1400
Hf	2
I	20
In	0.5
K	900
La	0.3
Mn	12
Na	600
Sb	0.3
Sc	0.2
Se	15
Sm	0.1
Th	2
Ti	500
V	5
Zn	100

Sartorius ones were deemed the best for the present studies. Upwards to 28 elements have been determined with detection limits ranging from 0.1 ng for samarium to 1400 ng for iron. Typically a ten hour irradiation (7×10^{12} n.cm²/sec) and a three hour counting period was necessary to achieve good sensitivities. Decay times varied from 2-3 days for the medium-lived nuclides (e.g. As, Sb etc.) and 2-3 weeks for the longer-lived ones (e.g. Cr, Fe, Zn, etc.). Selenium could be determined using a very short-lived nuclide of 17.4 seconds (^{77m}Se) or the longer-lived ⁷⁵Se nuclide. Once again the use of a high efficiency detector (with excellent resolution) and a prolonged irradiation time will yield the sensitivities required to determine the elemental concentrations from a rural or remote region.

QUALITY CONTROL

Unfortunately many papers have appeared determining trace elements in rainwater with little to show for quality control (e.g. blanks, blind replicates, use of certified reference material etc.). One crucially important aspect that has been maintained at our laboratory is the use of certified reference material. Both National Bureau of Standards water standard 1643a and 1643b and simulated rainwater 8409-1 have been employed along with the soluble rainwater analysis. Results for NBS 1643b are presented in Table 6. As can be seen the agreement is very good. For the particulate matter NBS coal standards 1632a and 1632b were also used in the analysis. The agreement with those certified and information values given by NBS are also in very good agreement.

TABLE 6

TRACE ELEMENTS IN NBS WATER STANDARD 1643b AS DETERMINED
BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

<u>Element</u>	<u>INAA Value</u> (ng/g)	<u>Detection Limit</u> (ng/g)	<u>NBS Value</u> (ng/g)
Al	17±3	4	-
Br	6±1	5	-
As	62±3	3	(49)
Ba	(39±4)	50	44±2
Ca	37±1 (ppm)	0.3 (ppm)	35 (ppm)
Cl	4.47±0.15 (ppm)	0.06 (ppm)	-
Co	28±1	1	26±1
Cu	24±3	20	21.9±0.4
I	2.4±1.0	2	-
K	1.71±0.12 (ppm)	0.4 (ppm)	(3) (ppm)
Mg	9.9±0.2 (ppm)	0.4 (ppm)	(15) (ppm)
Mn	30±1	3	28±2
Na	9.1±0.3	0.07	(8)
Sr	224±7	110	227±6
V	47±3	0.2	45.2±0.4

AREAS OF IMPROVEMENT

One technique, namely epithermal NAA, has enjoyed success in air filter analysis particularly for silver, iodine, indium, nickel and fluorine. This should be investigated to determine if the same can be done for rainwater and particulate matter and to further improve sensitivities over conventional thermal NAA. Work can also be done using freeze-drying methods and a better comprehensive list of elements must be investigated. Short-lived ^{77m}Se is one nuclide which has almost never been investigated in rain or snow water and also warrants investigation. Both cyclic and anti-Compton suppression methods can also be used to further lower the detection limits. Prompt-gamma ray activation analysis has also enjoyed excellent success in the recent past (Failey et al., 1979) and this method should be extended to rainwater particulate matter studies. Elements which have good potential for analysis include boron, sulphur and cadmium.

Certainly, the last chapter on the analysis of atmospheric precipitation chemistry has not been written as yet, and one can be confident that neutron activation analysis can play an important and leading role in this field of research.

REFERENCES

- Barrie, L.A. and Walmsley, J.L. (1978). Atmos. Environ. 12, 2321-2332.
- Beavington, F. and Cawse, P.A. (1979). Sci. Tot. Environ. 13, 263-274.
- Bogen, J. (1973). Atmos. Environ. 8, 835-844.

Boutron, C. (1979a). *Anal. Chim. Acta* 106, 127-130.

Boutron, C. (1979b). *Geophys. Res. Lett.* 43, 1253-1258.

Campbell, G.C., Stokes, P.M. and Galloway, J.N. (1985). "Acid Deposition, Effects on Geochemical Cycling and Biological Availability of Trace Elements", Subgroup on Metals of the Tri-Academy Committee on Acid Deposition, National Academy Press, Washington, D.C.

Cawse, P.A. (1975-1978, 1980-1981). "A Survey of Atmospheric Trace Elements in the U.K.: Results for 1974-1979)." Atomic Energy Research Establishment, AERE-R 8038, 8398, 8869, 9164, 9484, 9886.

Drake, J.J., Vermette, S.V. and Landsberger, S. (1986). *Water, Air and Soil Pollution*, (sent for publication)

Failey, M.P. et al. (1979). *Anal. Chem.* 51, 2209-2221.

Galloway, J.N. et al. (1982). *Atmos. Environ.* 16, 1677-1700.

Hamilton, E.P. and Chatt, A. (1982). *J. Radioanal. Radiochem.* 71, 29-45.

Landsberger, S., Jervis, R.E. and Balicki, A. (1985a). *Int. J. Environ. Anal. Chem.* 19, 219-225.

Landsberger, S., Jervis, R.E. and Monaro, S. (1985b). "Trace Analysis of Wet Atmospheric Deposition by Nuclear Methods", *Trace Analysis, Volume 4*, Academic Press, pp 237-291.

Landsberger, S. et al. (1983). Int. J. Environ. Anal. Chem. 16, 95-130.

Luten, J.B. (1976). Proc. Int. Conf. Mod. Trends. Act. Anal., Munich, pp 574-581.

Merritt, W.F. (1976). "Measurement, Detection and Control of Environmental Pollution", IAEA-SM-205/6, pp 75-87.

Pierson, D.H. et al. (1973). Nature 241, 252-256.

Rancitelli, L.A. and Perkins, R.W. (1970). J. Geophys. Res. 75, 3055-3064.

Salmon, L. (1975). "Instrumental Neutron Activation Analysis in Environmental Studies of Trace Elements", Atomic Energy Research Establishment, AERE-R 7859.

Schuyster, P., Maenhaut, W. and Dams, R. (1978). Anal. Chim. Acta 100, 75-85.

Slanina, J. et al. (1979a). Int. J. Environ. Anal. Chem. 6, 67-81.

Slanina, J. et al. (1979b). Int. J. Environ. Anal. Chem. 7, 161-176.

Tanner, T. M., Rancitelli, L.A. and Haller, W.A. (1972). Water, Air and Soil Pollut. 1, 132-143.

INTEGRATED CONCLUSIONS OF THE WORKING GROUPS

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The list of metals considered included Pb, Cd, Hg, Ni, Cu, As, Se, Zn, V, Cr Mn, In, Ge, Sb, Sn, and Ag.

1. Question

If routine sampling is defined as a field operation using a wet-only collector, semi-technical labor with one site visit per day and only simple sample preservation and handling procedures conducted on-site, then for which elements can one perform routine measurements in precipitation of: (i) total metal concentration; (ii) metal species concentration and soluble and insoluble metal concentrations? It was emphasized that an affirmative answer should be given only if an accurate routine measurement with similar field facilities to those proposed above had been made for an extended period.

Response

Both groups concluded that measurement of metal species concentrations and insoluble/soluble concentrations were more suited to special intensive research than to routine networks. However, total concentrations of many of the metals can be measured routinely by networks if appropriate sample collection, handling and analysis procedure are followed. Table 1 summarized information on the concentration, required detection limit and appropriate analytical method for those metals deemed suitable for routine measurement. Metals not suited to routine measurement are Hg, In, Ge, Sb, Sn and Ag. If pre-concentration of the sample is to be avoided, as was recommended by the working groups, the most appropriate method of analysis for most samples is graphite furnace atomic absorption with a multiple injection capability. Anodic voltaic stripping was an equally good choice for many metals including the biologically harmful Pb and Cd. Inductively coupled plasma emission spectroscopy and neutron activation analysis have the advantage of being a multi-elemental technique, but the disadvantage of insensitivity. With pre-concentration by a hundred-fold, however, they become practical alternatives.

2. Question

Collector

The precipitation sampler should be an automatic wet-only sampler with metal-free surfaces and a tight seal between lid and bucket. It should be dedicated to the collection of samples for metal analysis. If pre-cleaned in a central laboratory, bag liners could be used. Several rigorous cleaning procedures are outlined in the papers of these proceedings. It should be emphasized that a thorough evaluation of the container preparation procedure should be done to optimize the amount of labor involved.

QC Procedures

A rigorous quality control program must be established with field blanks, co-located samplers, split samples and blind certified reference material samples playing an integral role in yielding routine information on the precision and accuracy of a measurement. Uncertainties associated with contamination in the field may be greater than those introduced in the analysis step. This fact should be recognized in the design of the QC/QA program.

Sample Handling and Preservation

Sample handling with respect to insoluble particulate matter and sample preservation procedures were topics of considerable discussion. On the one hand was the opinion that it was desirable to introduce some measure of uniformity into the handling of samples by not adding acid until they arrived in the laboratory, then adding acid, shaking well and allowing to settle for a fixed period of time before extracting an aliquot for analysis. Critics of this procedure claimed that failing to acidify in the field can result in irreversible adsorption of metals on the container walls. Acidification in the field with HNO_3 (rather than HCl) immediately after collection to a pH of 1-1.5 seems to be the most favored approach. It should be emphasized that insoluble particles contribute substantially to the total concentration of some metals in solution. The current practice of extracting a 'representative' sample of soluble and insoluble metals is by no means without possible bias related to how the sample was mixed before analysis and to irreversible adsorption of particles to container walls. Research is needed to resolve such uncertainties. Fortunately many anthropogenic metals are predominantly in fine particle-acid soluble form and therefore are not sensitive to this source of uncertainty.

Analysis

If possible, the analytical technique should be chosen to avoid pre-concentration of the sample which can be another source of contamination. Graphite furnace atomic adsorption and the anodic voltaic stripping technique are the most suited to precipitation analysis although inductively coupled plasma mass spectroscopy may be an equally powerful multi-elemental technique available in the next five years. Neutron activation analysis has the advantage that it measures total concentrations in solution whereas tests have to be run to demonstrate that other techniques are not missing an insoluble fraction. The disadvantage of neutron activation analysis is its insensitivity requiring at least 20 fold pre-concentration step which adds to the change of error.

TABLE 1. A list of metals whose concentrations can be measured routinely as well as a summary of the range R and mean concentration C(μ g/L) expected in precipitation of rural to remote areas, the required analytical detection limit ADL (μ g/L) at 95% confidence level (25) and an indication of which analytical method is best suited to the measurement. INAA - instrumental neutron activation analysis; GFAA - graphite furnace atomic absorption; AVS - anodic voltaic stripping; ICP-inductively couple mission spectroscopy.

METAL	R (μ g/L)	C (μ g/L)	ADL (μ g/L)	ANALYTICAL TECHNIQUE			ICP
				INAA	GFAA	AVS	
Pb	0.1-20	3	0.05	N	Y	Y	Y(20)
Cd	0.05-0.2	0.1	0.02	N	Y	Y	Y(100)
Ni	0.20-1.0	-	0.10	N	Y	Y	N
Cu	0.10-20	-	0.10	Y(20)	Y	Y	Y(100)
As	0.10-1.0	-	0.05	Y(20)	Y(!)	N	Y(100)
Se	0.04-0.4	-	0.02	N	N	Y	N
Zn	1.0-20	5	0.5	Y(100)	Y	Y	Y(20)
VC	0.1-30	1	0.05	Y	Y(*)	N	Y(100)
Cr	0.1-30	1	0.05	N	Y(*)	N	Y(100)
Mn	0.3-20	2	0.2	Y	Y	N	Y(100)

() brackets enclose the pre-concentration factor

! hydride generation

* multiple injection

INVITEES AND PARTICIPANTS AT THE WORKSHOP ON THE

ASSESSMENT OF RISKS TO PRECIPITATION

25-26 January 1988

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